hydrogens, are assigned to methyl groups at the 2 and 4 positions on the pyridine ring. The triplet centered at 2.02 p.p.m. (*e*) and the multiplet centered at 1.80 p.p.m. (*f*) are assigned to the two methylene hydrogens (*e*) and (*f*) on the basis of double and triple resonance experiments. When either of the signals (*e*) or (*f*) are externally irradiated, the signal at 2.72 p.p.m. (*b*) simplifies to a doublet, and when (*e*) and (*f*) are simultaneously irradiated, (*b*) coalesces to a sharp singlet. Hence, (*b*) is coupled to both hydrogens (*e*) and (*f*) by the same value of 5 cps. These effects are reciprocal, for when (*b*) is irradiated (*e*) simplifies to a doublet, and (*f*) becomes sharper. The signals at 1.36 (*g*) and 1.16 p.p.m. (*h*), each equivalent to three hydrogens, are due to the *gem*-dimethyl groups at the 8 position. The signal at the unusually high field of 0.54 p.p.m. (*j*) is assigned to the methyl group at position 7a. The four other methylene hydrogens on the five-membered ring give signals in the area from 1.7 to 1.2 p.p.m. (*k*). The signals for the *gem*-dimethyl hydrogens are also in this area and partially obscure the signals of the four methylene hydrogens.

The spectral data presented are consistent with that postulated for 2,4,7a,8,8-pentamethylcyclopentapyrindan. This is the first compound of this type to be identified in petroleum.

Optical Activity of the Identified Compounds. A number of workers (*3, 12, 16*) have observed optical activity in petroleum fractions. Fenske *et al.* (*3*) studied the distribution of optical activity in distillation fractions of a number of crude oils. They reported that optical activity appears in petroleum distillates at molecular weights of approximately 220 and reaches a maximum at about 400 molecular weight. This optical activity is taken as supporting evidence that petroleum is formed from the remains of plants and, to a lesser extent perhaps, animals. The two compounds isolated from petroleum are optically active. The cyclohexylpyridine has a specific rotation of $(\alpha)_D^{27}$ −3.8°, and the specific rotation of the cyclopentapyrindan is $(\alpha)_D^{27}$ −2.0. The optical activity of these compounds is additional evidence in support of the theory that natural products, such as terpenoid-type compounds, are the source material of petroleum.

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Hydrolysis of Oil-Soluble Organic Amine Salts in the Two-Phase Water-Benzene System

M. A. SCHEIMAN and H. R. BAKER
Naval Research Laboratory, Washington, D. C. 20390

SMALL CONCENTRATIONS of high molecular weight organic salts are added to bulk-refined petroleum products to protect against the corrosive action of fresh or salt water generally found as subnascent phases in storage, transport, and handling facilities. These additives are preferentially adsorbed on ferrous metals or their oxide films to form a barrier that retards corrosion. Rust inhibitors for fuels should be of the ashless type exemplified by the ammonium or organic substituted ammonium salts of the high molecular weight sulfonic or carboxylic acids. Normally, only minor losses of the additive from the fuel should occur by processes other than adsorption on corrosion-susceptible surfaces. Field performance of commercially available salts has been erratic. Fuels rendered rust-inhibitive at their points of origin have rapidly lost that property through contact with the aqueous phase. The carbon dioxide concentration or the pH of the aqueous phase also affects the susceptibility of the inhibitor to water extraction.

The cations and anions of these ammonium salts in solution in an organic phase are, respectively, Brönsted acids and bases that are susceptible to attack by other bases or acids located in a contacting immiscible phase such as water. The stability and the retention of an ammonium salt in the organic phase depend on such factors as the intrinsic acid and base strengths of the proton donors and receptors in each phase, the effect of the phase dielectric constant on ionic activity, and the stability conferred on

Benzene solutions containing the water-insoluble products of reaction between a series of amines and phenylstearic or dinonylnaphthalenesulfonic acids were brought in contact with aqueous phases of varying pH and CO_2 content. The extent of reaction is reported as per cent hydrolysis—i.e., per cent nitrogen originally present in the organic phase that was transferred to the aqueous phase. Equilibrium constants for the reactions between aqueous phase acids and the methylammonium sulfonate were determined and found to reflect the aqueous phase acid strengths. The constant for carbonic acid indicates that it has a greater strength than formic acid. For the reaction between methylammonium sulfonate and aqueous phase hydronium ion to yield organic phase sulfonic acid and aqueous phase methylammonium ion the equilibrium constant, $K_{eq.}$, is 12.7 ± 0.6 and the standard free energy change, ΔG°, is $-(1.51 \pm 0.3)$ kcal. per mole of hydronium ions.

the reactive species by solvation effects. The complexity of these interrelationships and the limited data available for defining the effective parameters have precluded the design of salts that will be retained unchanged in the fuel until needed. To obtain such data the benzene-water system was chosen as a prototype and dinonylnaphthalenesulfonic and phenylstearic acids were taken as representatives of the wide variety of commercial sulfonic and naphthenic acids whose salts have been reported to be effective inhibitors (*1*).

The experimental work reported here explores the effects of anion base strength and cation structure on the retention of amine-organic acid salts in a hydrocarbon phase in contact with water, and the effect of such aqueous phase variables as acid and carbon dioxide concentrations.

EXPERIMENTAL

Chemicals. Dinonylnaphthalenesulfonic acid, H(DNNS) (King Organic Chemical Co., Norwalk, Conn.), received as a specially synthesized water-white acid, had a neutral equivalent of 502.9 (theoretical 460.7). This discrepancy results from the presence of some unsulfonated hydrocarbon in the product. Phenylstearic acid, H(ϕSt) (Hollingshead Corp., Camden, N. J.), had a neutral equivalent of 356.7 (theoretical, 360.6). Methylamine was obtained by the quantitative distillation of a strongly alkaline solution of reagent grade methylamine hydrochloride. Benzylamine, ϕ—CH_2—NH_2, and triisoamylamine, TIAA, of Eastman Kodak White Label grade were purified by passing CO_2-free nitrogen at the rate of 60 cc. per minute through the compounds for 2 hours. The equivalent weight of the ϕ—CH_2—NH_2 was 107.9 (theoretical 107.12) and of the TIAA was 232.0 (theoretical 227.4). All other solvents and compounds were of reagent grade and were used as received. Distilled water was stored, prior to use, in Ascarite-vented borosilicate glass bottles. When CO_2-free water was desired it was redistilled from an alkaline solution in an all-glass distillation apparatus that had been thoroughly flushed with nitrogen. The distillate had a pH of 6.7 at 25° C. All distilled water fractions were routinely tested for dissolved nitrogenous compounds; none were found.

Preparation of Ammonium Salts. The ammonium salts of H(DNNS) (*6*, *7*) and H(ϕSt) were prepared by adding stoichiometric quantities of the base to the acid. (For convenience all the reaction and/or association products resulting from the addition of a stoichiometric quantity of a nitrogenous base to an organic acid are referred to as ammonium salts.) The products ranged from glassy solids to viscous liquids. Since these salts were not in a physical state permitting further purification by usual methods, the impurity content of the reactants controlled that of the salts. The salts were dissolved in benzene to make 0.05 molal solutions and analyed before use. A one to one stoichiometric relationship was found between cation N (analytical uncertainty ±0.6%) and the carboxylate group (uncertainty ±0.9%). The method of preparing the H(DNNS) salts assured stoichiometry (*6*, *7*). The reaction product of methylamine and phenylstearic acid was unstable in the sense that the reaction product in the "dry" state and in benzene solution rapidly lost methylamine base to the vapor phase. Reactions involving this salt were performed with stoichiometric quantities of H(ϕSt) in the benzene phase and methylamine in the aqueous phase. Similar salts in organic liquid-water two-phase systems reach the same equilibrium position irrespective of the initial distribution of the salt or its components (*8*, *9*). Preliminary experiments in this investigation confirmed this finding.

Analytical Procedures. The salt concentration of a phase was assumed to be equal to the concentration of the organic nitrogen present. In the benzene phase the organic nitrogen concentration was determined by a standard micro-Kjeldahl analysis, while the total concentrations of all the Brönsted acids—e.g., ammonium ions, carboxylic, sulfonic, and other relatively strong acids which titrate to the same thymol blue end point—were determined by nonaqueous titration using 0.1*N* sodium methoxide in benzene (*4*). Where the benzene phase organic nitrogen was depleted by metathesis with the aqueous phase, the difference between the concentrations as determined by the Kjeldahl analysis and the sodium methoxide titration is reported as "free acid"—e.g., hydroxy acid not compensated by an equivalent of nitrogenous base. In general, acid concentration as determined by the titration procedure remained constant throughout the experiment, since H(DNNS), H(ϕSt), and their salts are not water-soluble. Increases in the concentrations of titratable acids during any run indicated the transfer of aqueous phase (Brönsted) acids to the benzene phase. A decrease in the concentration of benzene phase acids was always accompanied by a loss of benzene phase nitrogen and the formation, in the aqueous phase, of an oil-water emulsion.

Organic nitrogen base which entered the aqueous phase was determined by titrating with 0.01*N* H_2SO_4 to the Mas indicator end point. If the aqueous phase contained an oil-water emulsion, the total nitrogen content was determined by a micro-Kjeldahl analysis on a homogenized aliquot, while the water-soluble amine was titrated with H_2SO_4 from an aliquot of the clear centrifuged sample. Where the aqueous phase contained an excess of some initially added hydroxy acid—e.g., H_2SO_4—the micro-Kjeldahl method was used to determine ammonium ion concentration, while titration with 0.1*N* NaOH to the Mas indicator end point determined the uncombined or "free acid."

Table I. Stability of Benzene Solution of Ammonium Salts in Presence of Water and Carbon Dioxide[a]

	Benzene Phase				Aqueous Phase				
	Salt Concn.		Free Acid Concn.		N Concn.		pH		
Salt	Initial	Final	Initial	Final	Initial	Final	Initial	Final	% Hydrolysis
$CH_3—NH_3^+$ (DNNS)	56.7	54.9	0.0	0.3	0.0	0.4[b] 1.7	5.6	7.06	0.7[b] 3.0
$\phi—CH_2—NH_3^+$ (DNNS)$^-$	53.0	52.6	0.0	0.4	0.0	0.3	5.6	6.74	0.6
$(TIAA)^+$ (DNNS)$^-$	43.1	42.8	0.0	0.0	0.0	0.3	5.6	7.06	0.7
$CH_3—NH_3^+$ (ϕSt)$^-$	50.8	0.4	0.0	52.1	0.0	50.4	5.6	8.43	99.2
$\phi—CH_2—NH_3^+$ (ϕSt)$^-$	52.7	27.6	0.0	24.7	0.0	24.0	5.6	7.56	45.6
(TIAA) (ϕSt)	49.9	48.6	0.0	1.2	0.0	1.0	5.6	7.71	2.0

[a] Concentrations expressed in terms of millimoles per 1000 grams of solution. [b] Emulsion formed. Lower value represents nonemulsion N.

Experimental Procedure. The hydrolytic stabilities of the methylamine, benzylamine, and triisoamylamine salts of H(DNNS) and H(ϕSt) in the presence of carbon dioxide were determined by equilibrating 30 grams of 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 cc. per minute 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 2 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 to 1 (weight) mixture of water and benzene, the separation and removal process was repeated, and the total weight of each phase recovered was recorded. Gravimetric aliquots of the benzene and water phases were analyzed for the reaction products and the results reported in terms of millimoles per 1000 grams of solution. 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 CO_2-free N_2. The phases were brought into contact by magnetic stirring for 3 hours, following which the system was permitted to equilibrate undisturbed for 5 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 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 I and IV).

To assure reproducibility, each experiment was performed twice with two analyses per experiment and the results of the four analytical determinations were averaged. A materials balance was kept on each experiment—e.g., whether 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 the starting solute concentration were found in any set of experiments (see Table I). The relative salt hydrolytic instability in any system, reported as per cent hydrolysis in Tables I and IV, represents the fraction of the total nitrogen originally present in the benzene phase that has transferred to the aqueous phase.

RESULTS AND DISCUSSION

The results of the equilibration studies of methylamine, benzylamine, and triisoamylamine salts of H(DNNS) and H(ϕSt) in the benzene-water system saturated with carbon dioxide are presented in Table I.

As a class the salts of H(DNNS) displayed excellent hydrolytic stability in this test. Approximately 0.6% of the salt in the benzene phase underwent hydrolysis. Nitrogen base entering the aqueous phase, where its reaction product with CO_2 increased the phase pH from 5.6 to a less corrosive 7.0, left "free" H(DNNS) in the organic phase. The apparent discrepancy between amine transferred to the water phase and free acid remaining in the organic phase is not greater than the experimental uncertainty of the free acid determination, which represents a small difference between the two large experimental quantities. The methylamine salt lost 2.3% of the initial salt concentration to an oil-water emulsion in the aqueous phase. Losses to the emulsion interface represent a second mechanism for the depletion of inhibitor from the organic phase. Such losses may be expected in pipeline and tanker operations; they have one possible advantage, in that they provide a mechanism whereby water-insoluble corrosion inhibitors could penetrate a subnatant aqueous layer to reach and protect underlying metal. However, an adequate concentration of the additive should be present to provide a reserve buffer against the continuous depleting effect of repeated contacts with new aqueous phases during transportation. The methylammonium salts of H(DNNS) did not form emulsions when the initial pH of the aqueous phase was less than 4.0.

The hydrolytic stabilities of the organic phase ammonium phenyl stearate salts in the presence of carbon dioxide and an aqueous phase follow an order that appears to be predictable from the solubilities of the amines and their acid conjugates, and from the acid dissociation constant of the associated organic acids (Table II). It would, however, be misleading to assume that the relative solubilities control the distribution that has been found. To demonstrate that H(ϕSt) can chemically retain an amine in the benzene phase, the behavior of 0.05*M* benzylamine (very soluble in both water and benzene) was examined by distribution experiments in the absence of CO_2, in the presence of 1 atm. of CO_2, and in the presence of 1 atm. of CO_2 and 0.05*M* H(ϕSt) in the benzene phase (Table III). Constants of formation, K_f, between an amine and a carboxylic acid to form the corresponding ammonium carboxylate in low dielectric constant organic liquids range from 100 to 1000 (*2*, *11*). Thus a 0.05 molal amine carboxylate salt solution could contain 36 to 13% of the stoichiometric salt quantity as unreacted acid and amine. Carbon

Table II. Physical Properties of Amine Salt Acid and Base Conjugates

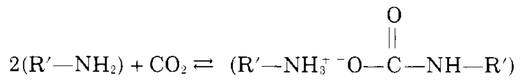
Acid or Base	Molecular Weight	K_a or K_b	Water Solubility		Benzene Solubility
			Acid form	Base form	
Methylamine	32.16	4.32×10^{-4}	V.S.	959 l./l. H_2O	33 l./l. ϕH
Benzylamine	108.15	2.35×10^{-5}	V.S.	∞	∞
Triisoamylamine	228.4	7×10^{-4}	<10 ^{2}mole/l.	<10 ^{4}mole/l.	∞
Phenylstearic acid	360.6	$K_a \approx 10^{-5}$	Insol.	Insol.	V.S.
Dinonylnaphthalenesulfonic acid	460.7	$K_a > 0.2$	Insol.	Insol.	V.S.

Table III. Nitrogen Distribution Ratio between Water and Benzene Phase for 0.05 Molal Benzylamine in Presence and Absence of CO_2 and $H(\phi St)$

(0.05-molal ϕH soln.)

	Type of System	$H_2O/\phi H$ Distribution Ratio
1.	$\phi—CH_2—NH_2$	0.21
2.	$\phi—CH_2—NH_2 + CO_2$	7.42
3.	$\phi—CH_2—NH_2 + CO_2 + H(\phi St)$	0.83

dioxide reacts directly with free amine to form the corresponding ammonium carbamate (*13*) according to Reaction 1.



$$2(R'—NH_2) + CO_2 \rightleftharpoons (R'—NH_3^+ \, ^-O—\overset{\overset{O}{\|}}{C}—NH—R') \qquad (1)$$

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 low aqueous phase solubilities.

The phase distributions of 0.05 molal solutions of the methylammonium salts of $H(\phi St)$ and H(DNNS) were tested in the absence of carbon dioxide. The two phases in the methylamine-phenyl stearate system spontaneously merged, in an exothermic reaction, to form an unbreakable emulsion. However, after saturation with carbon dioxide, the emulsion broke and the phases separated. The (emulsion) phase pH fell from 10.0 to approximately 8.8 (aqueous phase) during the gas saturation period. In the absence of CO_2, 0.3% of the methylammonium (DNNS) was hydrolyzed, while 2.2% of the salt entered the aqueous phase as part of an oil-water emulsion.

A re-examination of the above results leads to the postulate that hydrated carbon dioxide reacts with the sulfonate and carboxylate salts by a metathetical process of acid displacement—e.g., the result of the competitive reaction between the anion conjugates of acids HA_a and HA_b for a proton according to

$$HA_a + A_b^- \rightleftharpoons A_a^- + HA_b \qquad (2)$$

If the process occurs in a two-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), the reaction may be considered an interphase ion exchange. The results of the ion exchange between organic phase methylammonium (DNNS) and aqueous phase hydronium ion-anion conjugate pair, part of an investigation into the acid displacement mechanism, are presented in Table IV and Figure 1. The aqueous phase acid concentrations are those of the analytically determined undissociated acid, HA. No evidence for the transfer of aqueous phase acid to the organic phase at equilibrium was found. In Figure 1 the relationship between the extent of ion exchange, reported as per cent hydrolysis in Table IV, and the equilibrium aqueous phase hydronium ion concentration at 25° C., expressed in pH units, is

$$\log (\% \text{ hydrolysis}) = 2.08 - 0.34 \text{ (pH)} \qquad (3)$$

The mass action relationship, represented by Figure 1, conforms to

$$\log \frac{[CH_3—NH_3^+]_a}{[R—SO_3^- \, ^+H_3N—CH_3]_o} = \log \frac{[R—SO_3H]_o}{[R—SO_3^- \, ^+H_3N—CH_3]_o} = (0.472 \pm 0.46) \log [H_3O^+]_a + (0.530 \pm 0.032) \qquad (4)$$

$$K'_{eq} = \frac{[CH_3—NH_3^+]_a}{[R—SO_3^- \, ^+H_3N—CH_3]_o[H_3O^+]_a^{0.47}} = \frac{[R—SO_3H]_o}{[R—SO_3^- \, ^+H_3N—CH_3]_o[H_3O^+]_a^{0.47}} = 3.40 \pm 0.26 \qquad (5)$$

In Figure 1 the ordinate may represent either the concentra-

Table IV. Acid Displacement of Methylammonium Dinonylnaphthalene Sulfonate as a Function of Aqueous Phase Acid Concentration[a]

	Aqueous Phase				Benzene Phase			
Acid	Initial concn.	Equilibrium concn.	Equilibrium H_3O^+	Equilibrium N concn.	Initial salt concn.	Final salt concn.	Equil. free acid	% hydrolysis
HOH	2×10^{-3}	3×10^{-4}	3×10^{-4}	0.17	56.7	56.7	N.D.[b]	0.3[c] 2.5
H_2CO_3	0.07	2×10^{-4}	9×10^{-5}	0.40	56.7	56.7	N.D.[b]	0.7[c] 3.1
$CH_3—CO_2H$	49.5	46.0	0.23	3.5	55.9	52.5	3.5	6.1
HCO_2H	51.9	45.8	1.25	6.1	55.6	49.4	6.2	11.9
H_2SO_4	25.8	17.2	19.6	17.2	52.7	35.3	17.1	33.2
H_2SO_4	53.6	42.5	41.6	22.2	52.7	30.5	22.2	42.2

[a] All concentrations expressed in terms of millimoles per 1000 grams of solution. [b] N.D. Nondetectable. [c] Emulsion formation. Smaller value represents nitrogen in true aqueous solution.

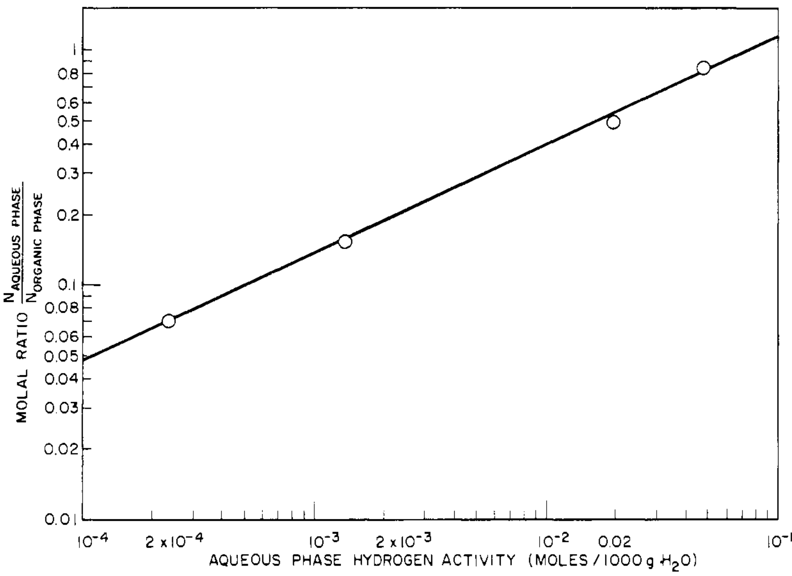


Figure 1. Amine distribution as a function of equilibrium H_3O^+ concentration in aqueous phase

tion 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 measured hydronium ion activity.

The equilibrium constant, K_{eq}, and the standard free energy change, $\Delta G°$, for the ion-exchange reaction, derived by multiplying both parts of Equation 5 together to yield $(K'_{eq})^2$, are

$$(K'_{eq})^2 = K_{eq} = \frac{[R{-}SO_3H]_o[CH_3{-}NH_3^+]_a}{[\text{salt}]_o^2[H_3O^+]_a} = 11.57 \pm 1.77 \qquad (6)$$

and

$$\Delta G° = 1.45 \pm 0.09 \text{ kcal. per mole}$$

The value of K_{eq} obtained when Equation 6 was calculated from the experimentally determined reactant and product equilibrium concentrations was 12.7 ± 0.7, and $\Delta G°$ equaled $-(1.51 \pm 0.03)$ kcal. per mole. A constant value for K_{eq} cannot be obtained if the salt concentration in the denominator of Equation 6 is not squared. Recent investigations in this laboratory on the conductometric behavior of salts of H(DNNS) in organic solvents of low dielectric constant have suggested that a free H(DNNS) molecule complexes with and stabilizes a salt molecule (*15*). The over-all reaction of Equation 6 may be represented conditionally as

$$2(R{-}SO_3^{-}\,{}^{+}H_3N{-}CH_3)_o + (H_3O^+)_a \rightleftarrows$$
$$\{(R{-}SO_3H)\cdot(\text{salt})\}_o + (CH_3{-}NH_3^{-})_a \qquad (7)$$

The distribution coefficient for methylamine between aqueous and benzene phases has been reported (*5*) to be 20 and the free energy change for the isoelectronic aqueous phase reaction between methylamine and H_3O^+

$$CH_3{-}NH_3^+ + H_2O \rightleftarrows CH_3{-}NH_2 + H_3O^+ \qquad (8)$$

has been reported to be 14.5 kcal. per mole (*3*). Upon adding Equations 7 and 8 and adjusting the resulting equation to reflect the 20-fold decrease in organic phase methylamine, the benzene phase formation constant, K_f, and standard free energy of salt formation of Equation 7 can be calculated,

$$(CH_3{-}NH_2)_o + \{(R{-}SO_3H)(\text{salt})\}_o \rightleftarrows 2(R{-}SO_3^{-}\,{}^{+}H_3N{-}CH_3)_o \quad (9)$$

$$K_f = 6.84 \times 10^{10}$$
$$\Delta G° = -14.8 \text{ kcal. per mole}$$

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

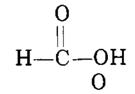
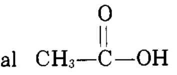
$$K_f = \frac{[R{-}SO_3^{-}\,{}^{+}H_3N{-}CH_3]_o^2}{[(R{-}SO_3H)(\text{salt})]_o[CH_3{-}NH_2]_o} = (7.29 \pm 0.16) \times 10^{10} \quad (10)$$

is −14.8 kcal. per mole. For comparison, the calculated formation constant and free energy decrease of a methylamine carboxylate in water are of the order of 4.32 × 10^5 and −7.7 kcal. per mole, respectively.

If the acid displacement mechanism is regarded as a measure of the competitive ability of an aqueous phase acid, HA (considered as an undissociated molecule), or its anion conjugate either to donate or accept a proton from an organic phase conjugate pair according to

$$(R{-}SO_3^-)_o + (HA)_a \rightleftarrows (R{-}SO_3H)_o + (A^-)_a \qquad (11)$$

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

$$\begin{aligned} K_{eq} = \frac{[R{-}SO_3H]_o[A^-]_a}{[R{-}SO_3^-]_o^2[HA]_a} &= 12.3 \text{ for } 0.05 \text{ molal } H_2SO_7 \\ &= 13.7 \text{ for } 0.025 \text{ molal } H_2SO_4 \\ &= 0.76 \text{ for satd. } H_2CO_3 \ (7 \times 10^{-5} \text{ molal}) \\ &= 0.33 \text{ for } 0.05 \text{ molal } H{-}\overset{\overset{O}{\|}}{C}{-}OH \\ &= 0.092 \text{ for } 0.05 \text{ molal } CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH \end{aligned}$$

The anomalous position of H_2CO_3 in the series indicates that H_2CO_3 is a stronger acid than acetic acid (K_A = 1.78 × 10^{-5}). Recent investigations (*10, 12, 14, 16*) have indicated that equilibrium constant K_{CO_2} between CO_2 and its hydrated form H_2CO_3 in water is

$$K_{CO_2} = \frac{[CO_2]}{[H_2CO_3]} = 720$$

that the first dissociation constant, expressed as a function of $[CO_2 + H_2CO_3]$, is

$$K'_1 = \frac{[H_3O^+][HCO_3^-]}{[CO_2 + H_2CO_3]} = 4.30 \times 10^{-7}$$

and that the true K_1 of H_2CO_3 is

$$K_1 = \frac{[H_3O^+][HCO_3^-]}{[H_2CO_3]} = 1.7 \times 10^{-4}$$

Since the H_2CO_3 concentration in water is a function of the sparingly soluble CO_2 concentration (0.503 molal), a weaker acid will displace HCO_3^- from its salt at low pH values (by swamping the system with H_3O^+); however, at higher pH values and in the presence of a reserve buffer of CO_2, carbonic acid will displace the acid conjugate of a weaker acid. This effect is further enhanced, in the present investigation, by the ability of CO_2 to deplete further the free amine concentration in the benzene phase by forming carbamates.

NOMENCLATURE

H(DNNS), (DNNS) = Dinonylnaphthalenesulfonic acid and anion
H(ϕSt), (ϕSt) = phenylstearic acid and phenylstearate anion
$\phi—CH_2—NH_2$ = benzylamine
(TIAA) = triisoamylamine
$\Delta G°$ = standard free energy change
[salt] = molal concentration of methylammonium (DNNS)
$[H_3O^-]$ = aqueous phase hydronium ion activity
K_{eq} = equilibrium constant due to either dissociation or metathesis
K_f = equilibrium constant of formation of salt from its corresponding acid and base
K_a K_b = acid and base dissociation constants
K_1 = first dissociation constant of a multiprotic acid

Subscripts

a = dissolved in aqueous phase
o = dissolved in organic phase
R = dinonylnaphthalene radical
R′ = organic radical bonded to a functional group

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Relative Enthalpies of Sea Salt Solutions at 25° C.

LEROY A. BROMLEY
Department of Chemical Engineering, University of California, Berkeley, Calif. 94720

Heats of dilution and concentration of sea water have been measured at 25° C. These values have been correlated by use of extended Debye-Hückel theory. Values of the relative, apparent, and partial enthalpies of sea salts and water have been calculated. Although small, these values differ considerably from those for NaCl solutions.

In most calculations relating to sea water conversion, the heat effects are assumed to be negligible in separating water from sea salt solutions. Sometimes the heat effects are assumed to be the same as those of sodium chloride solutions.

The purpose of this paper is to examine these approximations, to report experimental measurements of the heat effects at 25° C., and to present correlations and tabulated values based on extended Debye-Hückel theory applied to these data.

THEORY

At very dilute concentrations, enthalpies of solutions may be calculated from Debye-Hückel theory, but deviations from this theory may be very large at concentrations above about 0.01 molal. Extended Debye-Hückel theory as presented by Lewis *et al.* (*1*) was modified slightly and used to correlate the data. The sea salts were treated as a single component, as was done for heat capacity (*2*). The standard states of zero enthalpy chosen at 25° C. are pure