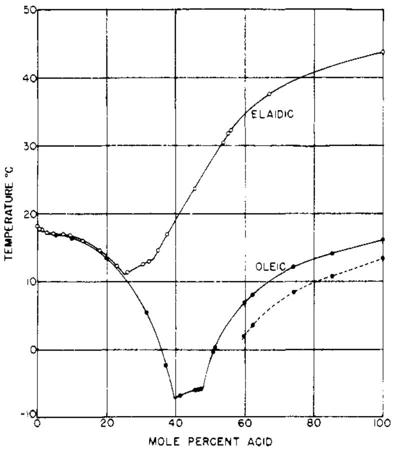

Figure 2. Binary freezing point diagrams for DMSO with oleic and elaidic acids

—— Stable equilibria

- - - - Metastable equilibria

in the elaidic acid system. Two freezing points were observed for compositions from 60 to 100% oleic acid, one for the unstable and the other for the stable modification of the acid.

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Solubilities and Activity Coefficients of Sodium Chloride and Potassium Chloride in Organic-Water Mixtures

Methyl(2-ethylhexyl)sulfoxide and Several Quaternary Ammonium Chlorides and Carboxylates Containing Water

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Organic-phase activity coefficients $\gamma_\pm^*$ or ratios $\Gamma = \gamma_\pm^*/\gamma_\pm$, which measure the selectivity of an organic liquid for extracting water in preference to salt, were determined for inorganic salts in a series of quaternary ammonium salts and in methyl(2-ethylhexyl)sulfoxide (MEHSO). Results support the previous generalization (from esters and amides) that the selectivity is controlled mainly by the water content of the organic-rich phase, but the selectivities with the present compounds are relatively low. In the absence of inorganic salts, saturation mole ratios of water to quaternary salt at 25° C. ranged from 2 to 15 (up to 28 wt. % of water), increasing with decreasing molecular weight and with decreasing symmetry. Saturated MEHSO contained 57 wt. % of water at 25° C., with only 1.7 wt. % of MEHSO in the water-rich phase; mutual solubility increased to a lower consolute point at 8° C. and 86 wt. % of water.

As a part of a water research program directed toward a better understanding of selective hyperfiltration membrane behavior, the selectivity of a dialkylsulfoxide and of a series of quaternary ammonium salts for water over inorganic salts was examined by measuring the activity coefficients of sodium and potassium chlorides, via solubilities and liquid-liquid distributions. The principal objective was to test extension of the generalities previously observed for both esters (*2*) and amides (*1*) to still different types of organic compounds. The quaternary ammonium salts were varied in regard to both structure and equivalent concentration, in the hope of finding either unusually high selectivity for water over salt, or reversal to a useful selectivity for salt over water. The results do support the previous generalization that the selectivity for water over salt is controlled mainly by the water content of the organic-rich phase, and they show some consistent dependence of water capacity on structure. However, the selectivities for water over salt were relatively low, and no instance of selectivity for salt over water was found.

The sulfoxide was examined because in the course of a study of metal-ion extractions by a series of dialkylsulfoxides (*3*), this one compound, the unsymmetrical methyl(2-ethylhexyl)sulfoxide (C_8H_{17}-SO-CH_3, MEHSO), was observed to dissolve a considerable amount of water although not itself very soluble in water.

EXPERIMENTAL

Solubility of water in the quaternary ammonium salts was measured in liquid-liquid equilibrations with inorganic salt absent, present at tracer concentration, or present at saturation. Solubility of the inorganic salt in the organic phases was also measured (by means of radioactive tracer) in the latter liquid-liquid equilibrations. When the water content of the organic phases was limited to less than saturation, the inorganic salt solubility was measured by saturation in slow flow through a salt-packed column. Quaternary ammonium salt solubilities in the water-rich phases were determined in separate equilibrations with consecutive increments of the organic salt until a visible excess (<0.01 ml.) remained undissolved. Details of these methods were reported (*1*). MEHSO-in-water and water-in-MEHSO solubilities were determined by measuring cloud-point temperatures.

Tracers ^{24}Na and ^{42}K were obtained first from the ORNL Radioisotopes Division and later were prepared by special irradiation. The quaternary ammonium cations and the carboxylate anions are identified in Tables I and II. Aliquat 336 and Aliquat 204 were obtained from General Mills, Inc., the other quaternary ammonium chlorides and the pivalic and ethylbutyric acids from Eastman Organic Chemicals, the abietic acid from Arizona Chemical Co., and the neodecanoic acid from Enjay Chemical Co. The two ester-acids were prepared at ORNL by alcoholysis of the acid anhydrides. Aliquat 336 chloride in petroleum ether was scrubbed with about 50 volumes of 0.01*M* HCl solution and then with water to remove any significant water-soluble fraction, then was recovered in a rotary vacuum evaporator. Its equivalent weight and selectivity performance were not significantly changed. The other reagents were used as received. The quaternary ammonium carboxylates QA were prepared by dissolving the calculated amounts of QCl and KA separately in petroleum ether (or benzene), mixing the solutions to precipitate KCl, and evaporating. Approximately 2% excess QCl was used to ensure that there would be no excess of A^-. Preliminary tests showed that replacement of up to 5 wt. % of QA by QCl had little effect on the uptake of tracer-tagged sodium ion, while, as expected, a slight excess of A^- increased it significantly. MEHSO was prepared both from reaction of methyl iodide with 2-ethylhexyl mercaptan and of methyl mercaptan with 2-ethylhexyl iodide to produce methyl(2-ethylhexyl)sulfide, followed by oxidation of the sulfide in glacial acetic acid with 30% hydrogen peroxide. The products were recovered by vacuum distillation with a small Vigreux column, b.p. 135° C. at 12 mm. Di-*n*-butylsulfoxide was prepared similarly.

Table I. Quaternary Ammonium Salts (QA) and Dialkylsulfoxide (MEHSO) Saturated with Water; Distribution of NaCl and KCl at Tracer Concentrations; 25° C.

Initial[a] *M* Cpd.	Wt. % Cpd. in Aq. Phase	Wt. % Water in Org.-Rich Phase	Γ_{NaCl}	Γ_{KCl}
MEHSO: METHYL(2-ETHYLHEXYL)SULFOXIDE				
5.3	1.7	57	1.6	1.4
0.5	<0.2	4.3	170	120
0.1	<0.1	0.8	90	60
Q336-CL: METHYLTRIALKYLAMMONIUM[b] CHLORIDE				
● 1.9	0.04	22.1	1.8	1.5
✕● 1.0	0.02	8.3	3.1	2.4
✕● 0.4	<0.01	2.9	12.5	
Q336-HS: METHYLTRIALKYLAMMONIUM[b] HEPTADECYL SUCCINATE[c]				
○ 1.1	<0.01	16.9	2.2	2.0
✕○ 0.5		7.4	7.0	
Q336-HM: METHYLTRIALKYLAMMONIUM[b] HEPTADECYL MALEATE[c]				
◐ 1.1	<0.01	14.3	3.5	
✕◐ 0.4		4.9	27	
Q336-AB: METHYLTRIALKYLAMMONIUM[b] ABIETATE[d]				
◑ 1.1	<0.01	14.7	3.0	
✕◑ 0.5		6.3	18	
HEPT$_4$-CL: TETRA-*n*-HEPTYLAMMONIUM CHLORIDE				
■ 1.9	0.05	10.8	4.4	
HEPT$_4$-HS: TETRA-*n*-HEPTYLAMMONIUM HEPTADECYL SUCCINATE[c]				
□ 1.0	<0.01	8.4	10.4	
Q204-CL: DIMETHYLDILAURYLAMMONIUM CHLORIDE				
▲ 2.0	0.05	28.4	1.3	
Q204-HS: DIMETHYLDILAURYLAMMONIUM HEPTADECYL SUCCINATE[c]				
✕△ 0.7	<0.01	14.0	2.8	
16 ME$_3$-HS: *n*-HEXADECYLTRIMETHYLAMMONIUM HEPTADECYL SUCCINATE[c]				
✕▽ 0.5	<0.01	12.0	2.5	
OCT$_3$PR-HS: *n*-PROPYLTRI-*n*-OCTYLAMMONIUM HEPTADECYL SUCCINATE[c]				
✕◇ 0.5	<0.01	4.4	10	

[a] The marginal symbols identify the points plotted in Figure 3. X-marked symbols (✕●. etc.) indicate dilution with diethylbenzene to the molarity shown. [b] Aliquat 336 contains a random mixture of *n*-alkyls, principally octyl and decyl plus some hexyl and lauryl. [c] Monoester of dicarboxylic acid with 3,9-diethyltridecanol-5. [d] Mixture of abietic acid (90%) with some other closely similar rosin acids.

RESULTS AND DISCUSSION

The miscibility curve of MEHSO and water (Figure 1) confirms the highly one-sided solubility behavior previously suggested (*3*). At 25° C. there is 57 wt. % or 0.93 mole fraction water in MEHSO (mol. wt. 175.3), but only 1.7 wt. % or 0.002 mole fraction MEHSO in water. In comparison, the symmetrical analog di-*n*-butylsulfoxide, of slightly lower molecular weight (162.3) and considerable solubility in water (6 wt. %), dissolves only 5 wt. % water. Thus, the unsymmetrical structure of MEHSO is an important factor in the skewed miscibility gap. This is reminiscent of the pair of isomeric amides noted previously (*1*): Dimethyllauramide dissolved 17.4 wt. % water, while its isomer dipropyloctanamide dissolved only 2.35 wt. %.

Equilibrium Compositions. The initial conditions and equilibrium phase compositions are shown in Tables I and II. In each test, the organic phase was saturated with water, with salt (in the presence of limited amounts of water), or with both simultaneously. The water contents of MEHSO at different water activities are compared in Figure 2. Pure water is taken as the reference state for both phases, so that a_1 is the same in both phases at equilibrium. Values of a_1 for the various (binary) salt solutions are from tabulations of Robinson and Stokes (*4*). The MEHSO contents of the aqueous phases are so small (maximum, 0.002 mole fraction in water) that with at least approximate conformity to Raoult's law the effects on a_1 are negligible. Of the esters (*2*) and amides (*1*) previously reported, only two extracted enough salt ($MgCl_2$) for it to be a significant component in the organic-rich phase and to increase the extraction of water; in all of the other tests the values of a_1 *vs.* X_1 fell along a single smooth curve for each organic reagent, such as indicated by the dashed line in Figure 2. In contrast, MEHSO extracted a significant amount of every salt tested, and along with it, more water than would be proportional to a_1, so that the points are not aligned. This effect appears to be greatest with magnesium chloride and least with potassium chloride. Analogy with the amides (*1*) suggest that the effect should decrease and disappear with sulfoxides of higher molecular weight. It did disappear for sodium chloride and potassium chloride when the MEHSO was diluted with diethylbenzene (Table II), which is analogous to increasing the molecular weight of the sulfoxide.

Table II. Quaternary Ammonium Salts (QA) and Dialkylsulfoxide (MEHSO) Saturated with Salt or with Both Salt and Water; 25° C.

Initial[a] *M* Cpd.	Contacting[e] Phase	Organic-Rich Phase		
		Wt. % water	Wt. % salt	Γ salt
	MEHSO: METHYL(2-ETHYLHEXYLSULFOXIDE)			
5.3	Sat. NaCl	22	5.1	1.56
	Dry NaCl	11.3	0.9	4.2
		5.5	0.03	70
		3.9	0.010	145
		2.7	0.005	180
		1.8	0.004	155
	Sat. KCl	23	3.8	2.2
	Sat. LiCl	32	30	1.08
	Sat. $BaCl_2$	37	10	1.13
	Sat. $SrCl_2$	33	18	1.11
	Sat. $MgCl_2$	41	26	1.06
0.5	Sat. NaCl	1.6	0.003	180
	Dry NaCl	0.9	0.002	135
		0.6	0.002	100
		0.2	<0.001	75
	Sat. KCl	1.3	0.003	210
	Dry KCl	0.9	0.002	150
		0.5	0.001	100
		0.2	<0.001	80
0.1	Sat. NaCl	0.2	0.002	50
	Dry NaCl	0.2	0.001	55
	Sat. KCl	0.3	0.001	65
	Dry KCl	0.2	0.001	40
	Q336-CL: METHYLTRIALKYLAMMONIUM[b] CHLORIDE			
● 1.9	Sat. NaCl	15.0	1.12	1.45
	Dry NaCl	8.5	0.21	2.1
		5.2	0.030	3.3
		4.0	0.004	6.5
		3.5	0.002	7.4
		2.6	<0.001	11.5
		2.4		13
		2.0		18
		0.6		105
	Sat. KCl	17.3	0.48	2.5
	Dry KCl	9.6	0.093	3.0
		6.4	0.025	3.9
		5.1	0.081	5.3
		4.1	0.024	7.8
		3.4	0.012	8.9
		3.0	<0.001	10.3
		2.8		13
		0.9		55
✖ 1.0	Sat. NaCl	7.2	0.164	2.6
	Dry NaCl	4.4	0.013	5.5
		2.7	0.001	11.2
		2.0	<0.001	19
		1.7		25
		1.3		35
		1.2		40
		1.0		65
		0.4		110
	Sat. KCl	8.0	0.105	3.2
	Dry KCl	4.8	0.010	6.2
	Q336-CL: METHYLTRIALKYLAMMONIUM[b] CHLORIDE			
		3.4	0.002	10.0
		2.9	0.001	11.8
		2.5	<0.001	14
		2.0		20
		1.2[f]		42
✖ 0.4	Sat. NaCl	2.8	0.005	8.8
	Sat. KCl	2.8	0.003	10.9
	Q336-HS: METHYLTRIALKYLAMMONIUM[b] HEPTADECYL SUCCINATE[c]			
○ 1.1	Sat. NaCl	15.7	2.33	2.4
	Dry NaCl	5.0	0.151	12
	Sat. KCl	16.3	1.62	3.6
⊗ 0.5	Sat. NaCl	6.7	0.35	6.5
	Dry NaCl	2.2	0.003	230
	Q336-HM: METHYLTRIALKYLAMMONIUM[b] HEPTADECYL MALEATE[c]			
◐ 1.1	Sat. NaCl	12.6	1.38	3.3
	Dry NaCl	3.2	0.015	80
◐ 0.4	Sat. NaCl	4.4	0.065	25
	Dry NaCl	1.7	0.001	500
	Q336-AB: METHYLTRIALKYLAMMONIUM[b] ABIETATE[d]			
◑ 1.1	Sat. NaCl	12.5	1.49	3.0
	Dry NaCl	3.9	0.049	30
◑ 0.5	Sat. NaCl	5.4	0.115	17
	Dry NaCl	1.2	<0.001	600
	Q336-NEOD: METHYLTRIALKYLAMMONIUM[b] NEODECANATE[f]			
⊝ 1.4	Sat. NaCl	23.0	5.4	1.53
	Dry NaCl	2.7	0.028	35
	Q336-ETBU: METHYLTRIALKYLAMMONIUM[b] ETHYLBUTYRATE[f]			
⊖ 1.5	Sat. NaCl	24.9	6.1	1.47
	Dry NaCl	3.7	0.066	21
	Q336-PIV: METHYLTRIALKYLAMMONIUM[b] PIVALATE[f]			
◓ 1.6	Sat. NaCl	26.9	7.6	1.28
	Dry NaCl	4.1	0.115	13
	$HEPT_4$-CL: TETRA-*n*-HEPTYLAMMONIUM CHLORIDE			
■ 1.9	Sat. NaCl	7.7	0.027	5.1
	Dry NaCl	5.0	0.004	8.0
		1.8	<0.001	150
	$HEPT_4$-HS: TETRA-*n*-HEPTYLAMMONIUM HEPTADECYL SUCCINATE[c]			
□ 1.0	Sat. NaCl	7.1	0.26	9.8
	Dry NaCl	4.6	0.082	20
		1.5	0.001	400
	Q204-CL: DIMETHYLDILAURYLAMMONIUM CHLORIDE			
▲ 2.0	Sat. NaCl	23.6	4.0	1.15
	Dry NaCl	7.4	0.134	2.0
		0.9	<0.001	26
	Q204-HS: DIMETHYLDILAURYLAMMONIUM HEPTADECYL SUCCINATE[c]			
⧗ 0.7	Sat. NaCl	12.0	1.56	2.8
	Dry NaCl	3.2	0.058	22
		1.6	0.003	175
	OCT_3-PR-HS: *n*-PROPYLTRI-*n*-OCTYLAMMONIUM HEPTADECYL SUCCINATE[c]			
✧ 0.5	Sat. NaCl	3.0	0.084	13
	Dry NaCl	1.0	0.002	200

[a-d] See Table I. [e] "Sat. NaCl": saturated NaCl solution plus excess crystals; "Dry NaCl": NaCl crystals, with limited water content in the organic phase and no free aqueous phase. Wt. % organic cpd. in equilibrium aqueous phases: MEHSO: satd. $BaCl_2$, <0.4; satd. LiCl, <0.3; satd. $SrCl_2$, $MgCl_2$, <0.2; satd. NaCl, KCl, <0.1. Quaternary ammonium salts: <0.01 in each. [f] Pivalic acid = trimethylacetic acid; neodecanoic acid = dimethyl-*n*-hexylacetic acid; ethylbutyric acid = diethylacetic acid.

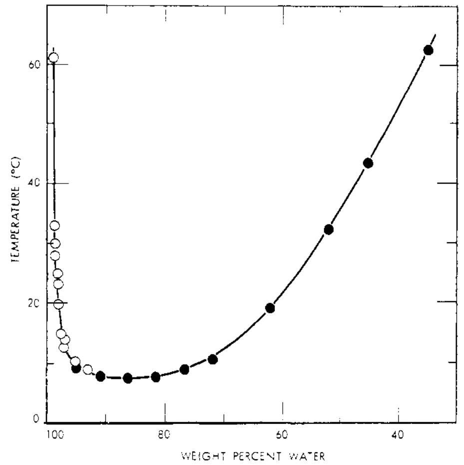

Figure 1. Miscibility curve of water-MEHSO from cloud-point temperatures

● Mixtures determined by weight

○ Mixtures determined by volume

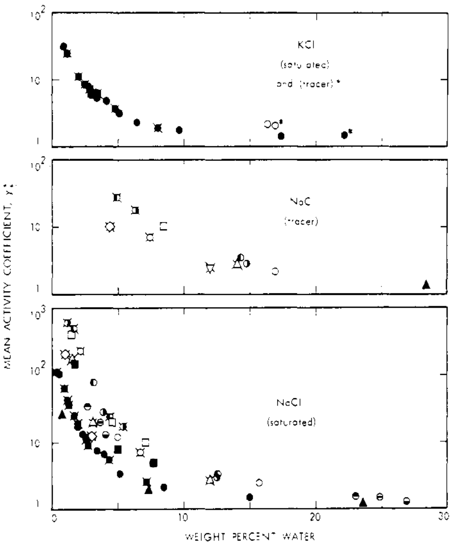

Figure 3. Variation of NaCl and KCl activity coefficients with water contents of quaternary ammonium chlorides (filled symbols) and carboxylates (open and shaded symbols)

X-marked symbols indicate dilution with diethylbenzene; individual symbols are identified in Tables I and II

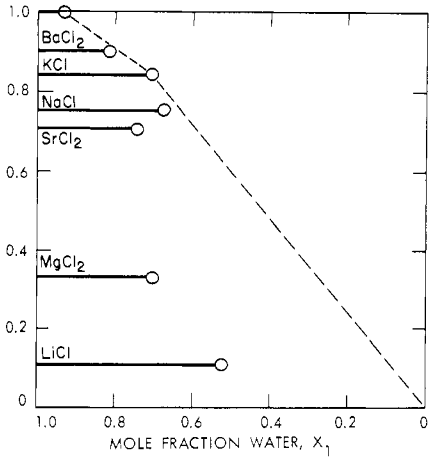

Figure 2. Activity of water in the two-phase water-MEHSO system, 25° C.

For the equilibria with saturated salts, the mole fraction of water is calculated as $m_{H_2O}/(m_{H_2O} + m_{MEHSO} + 3m_{BaCl_2})$, etc. If the salts are assumed to exist as ion clusters instead of dissociating, the corresponding mole fractions of water are higher, respectively, 0.86, 0.69, 0.70, 0.83, 0.84, and 0.66 for $BaCl_2$ to LiCl

In the the absence of inorganic salt, saturation mole ratios of water to quaternary salt ranged from around 2 to nearly 15 over the range of compounds tested. They increased with decreasing molecular weight of the quaternary ammonium salts and, at similar molecular weights, increased with increasing number of methyl groups around the quaternary nitrogen.

Salt Activity Coefficients. As previously (*1*), concentrations in each phase are expressed as moles of component per kilogram of water (*m*), even when water is itself only a minor component, and the activities in all phases are referred to the same standard state as in pure aqueous salt solution, providing the useful relation between activity coefficients and selectivity for water over salt

$$\Gamma = \gamma_{\pm}^*/\gamma_{\pm} = m/m^* = D(\text{water})/D(\text{salt}) \tag{1}$$

The activity coefficient ratio Γ is unity when water and inorganic salt are extracted equally well—i.e., when they are in the same ratio in both phases. Values of Γ greater than one represent preferential extraction of water; conversely, fractional values would represent preferential extraction of salt. In Equation 1, *D* is the distribution coefficient of the component indicated: D(salt) = [tracer counts per milliliter of organic phase] per [tracer counts per milliliter of aqueous phase]. For quaternary ammonium salts QA where A ≠ Cl (no common ion), at saturation with—e.g., NaCl, the mean activity coefficient

$$\gamma_{\pm}^* = (\gamma_{\pm} m_{\text{NaCl}})/m_{\text{NaCl}}^* \tag{2}$$

At tracer salt concentration

$$\Gamma = D(\text{water})/D(\text{NaCl}) \tag{3}$$

and $\gamma_{\pm}^* \approx \Gamma$ since $\gamma_{\pm} \approx 1$. For QCl (chloride common ion), at saturation with NaCl

$$\gamma_{\pm}^* = (\gamma_{\pm} m_{\text{NaCl}})/m_{\text{NaCl}}^*[1 + m_{\text{QCl}}^*/m_{\text{NaCl}}^*]^{1/2} \tag{4}$$

and at tracer NaCl concentration

$$\Gamma \approx [D(\text{water})\ m_{\text{NaCl}}/D(\text{Na})\ m_{\text{QCl}}^*]^{1/2} \tag{5}$$

Here m_{NaCl} must be estimated from the specific activity of the tracer solution, typically around 2×10^{-5} for ^{24}NaCl, and 5×10^{-4} for ^{42}KCl.

In the foregoing, the slight amount of the quaternary ammonium compound dissolved in the water-rich phase is assumed to have no significant effect on $\gamma_{\pm}$. If the effects of the larger but still small amounts of dissolved MEHSO on $\gamma_{\pm}$ in the water-rich phases are also negligible, then $\gamma_{\pm}^* \approx 0.588\ \Gamma$ for saturated potassium chloride, and $\gamma_{\pm}^* \approx \Gamma$ for saturated sodium chloride and for both salts at tracer concentrations in MEHSO. However, to avoid depending on that assumption, only the ratios Γ are reported for MEHSO.

As with the amides (*1*), the activity coefficients and activity coefficient ratios of the inorganic salts depend mainly on the water content of the organic phase, whether or not saturated with water. Dilution of a given reagent with a hydrocarbon has little effect on $\gamma_{\pm}^*$ or Γ, other than indirectly by the resulting decrease of the maximum water content. At a given water content for each quaternary ammonium salt, $\gamma_{\pm}^*$ is higher with the carboxylates than with the chloride. Between individual quaternary ammonium salts, $\gamma_{\pm}^*$ decreases slightly with increasing number of methyl groups. The shapes of the $\gamma_{\pm}^*$ *vs.* water content curves (Figure 3) are similar to those with dialkylamides (*1*), but they drop more sharply, and approach unity at lower water contents (at <5% *vs.* >10%) than did the amides. However, there is no suggestion of crossing the $\gamma_{\pm}^* = 1$ axis into a region of selective extraction of salt. The selectivity for water over salt by MEHSO almost disappeared at water contents above 30%, Γ being only slightly above unity. The maximum values of Γ, near 2% water, are around 200, much lower than the maxima obtained with several other compounds—e.g., 300 to 3000 for NaCl in several amides (*1*). It may be more appropriate, however, to consider these as rather high values of Γ for a compound having such a high water capacity as MEHSO does, suggesting that some homologs might show better combinations of salt rejection and water capacity.

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NOMENCLATURE

a_1 = activity coefficient of water (mole fraction scale, reference state pure water)
A = anion of quaternary ammonium salt
$D(s)$ = distribution coefficients $[s]_{org}/[s]_{aq}$ of the substance s
m_s = moles of the substance s per kilogram of water
Q^+ = quaternary ammonium cation
X_1 = mole fraction of water
$\gamma_\pm$ = mean activity coefficient of an inorganic salt (molality scale, reference state infinite dilution
Γ = activity coefficient ratio $\gamma_\pm{}^*/\gamma_\pm$
$*$ = refers to components in the organic-rich phase

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Heat of Formation of Sulfamic Acid

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The reaction of sulfamic acid with sodium nitrite has been investigated in both acidic and alkaline solutions. The reaction to yield nitrogen proceeds to a negligible extent in alkaline solution but is quantitative in acidic solution. Calorimetric measurements with acid solutions lead to values of ΔH_f° = -164.0_2 and -163.8_5 kcal. per mole for crystalline sulfamic acid.

MEASUREMENTS of the heat of reaction of sulfamic acid with sodium nitrite in alkaline solution have been reported (*6*), and the heat of formation has been calculated from the observed ΔH. Chernick (*1*) had previously measured the heat of reaction of sulfamic acid with sodium nitrite in acidic solution, but his results and derived heat of formation of sulfamic acid have not been published. Because there is a large discrepancy between the results of these earlier workers, new investigations of the reaction chemistry and thermochemistry of sulfamic acid have been carried out and form the basis for this report.

Experiments in both of the authors' laboratories confirm that the reaction between sulfamic acid and sodium nitrite does not proceed satisfactorily in the alkaline solutions used by Wu and Hepler (*6*) but does proceed quantitatively in various acidic solutions.

Chernick's measurements (*1*) in Manchester ($0.1N$ sulfuric acid as solvent) led to $\Delta H = -95.8$ kcal. per mole for the reaction that could be represented by

$$H_2NSO_3H(soln) + NaNO_2(c) = NaHSO_4(soln) + N_2(g) + H_2O(liq)$$

Preliminary measurements in Pittsburgh with conditions nearly the same as those used by Chernick led to $\Delta H = -95.3$ kcal. per mole for this reaction. The reaction proceeds equally readily in pure water as solvent, and the subsequent measurements reported here were made using purely aqueous sulfamic acid solutions.

EXPERIMENTAL

For the work done at the University of Manchester, B.D.H. microanalytical standard reagent sulfamic acid was used without further treatment. Sodium nitrite was B.D.H. AnalaR quality, and was recrystallized, dried, and stored in a desiccator prior to use. Volumetric analysis of the sample against permanganate indicated purity >99.9%. The reaction calorimeter, of the constant temperature environment type, has been described previously (*2*). The calorimeter was charged with a dilute solution of sulfamic acid (1081 grams of water and 6 mmoles of sulfamic acid), and the glass ampoule contained 3 mmoles of crystalline sodium nitrite. All heat measurements (*1*) are referred to 25° C.

For the work done at Carnegie-Mellon University, the sulfamic acid and the sodium nitrite were both Fisher Certified reagents and were purified as previously described (*6*). The calorimeter used for these measurements was patterned after one previously described (*3*). The calorimeter consisted of a Dewar vessel suspended in a brass can that was submerged in a water bath maintained at constant temperature. Temperatures were determined with a nickel resistance thermometer connected to a Leeds and Northrup Mueller G-2 Bridge and a Beckman Model 14 Breaker Amplifier. The resistance thermometer and manganin calibration heater were both contained in a glass spiral filled with mineral oil. For each measurement, a sample of crystalline sodium nitrite was introduced to a solution containing a two to fivefold excess of sulfamic acid. All measurements are referred to 25° C.

The calorimetric reaction investigated in Manchester can be represented precisely by the equation:

$$NaNO_2(c) + 2(NH_2SO_3H \cdot 10000\ H_2O) = N_2(g) + NaHSO_4 \cdot NH_2SO_3H \cdot 20001\ H_2O \qquad (1)$$

Results of five measurements lead to $\Delta H_1 = -96.94$ kcal. per mole (average deviation from mean ±0.09). The mean

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