complexes were only partially extracted by ether, resulting in a poor yield of molybdocyanide.

2. A quadrivalent molybdenum pyridine thiocyanate is almost completely precipitated in ammoniacal solution. By treatment of this with potassium cyanide a 70–75% yield of $K_4Mo(CN)_8 \cdot 2H_2O$ was obtained.

3. Quantitative yields of potassium molybdicyanide in solution were obtained by oxidizing potassium molybdocyanide with permanganate in acid solution and removing the manganese by oxidation to dioxide with permanganate after making the solution alkaline.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Studies on Hydrazine: Heats of Solution of Hydrazonium Salts at 25°. II

BY E. C. GILBERT AND V. C. BUSHNELL

The heat of solution of a number of hydrazonium salts has recently been reported from this Laboratory.[1] To complete the series the heats of solution of hydrazonium dibromide (anhydrous), hydrazonium sulfate, and hydrazonium dibromide (hydrated) have now been determined. That of the sulfate has also been determined by Bach[2] at a lower temperature.

Experimental

Apparatus.—The calorimeter was the same as previously used and the procedure was unchanged. It was again checked by measuring the heat of solution of sodium chloride.

Materials.—The salts were prepared from the free base and acids and purified by repeated crystallization. The anhydrous bromide was prepared from the hydrate by drying over phosphorus pentoxide. The preparation of the hydrate with exactly two molecules of water is somewhat difficult. It is very soluble in water and addition of nonaqueous solvents like alcohol removes one equivalent of acid, precipitating the monobromide. This peculiarity likewise precludes washing the crystals with anything but water. Forced drying practically always results in a slight loss either of water or hydrobromic acid. The samples used were analyzed both for hydrazine and for bromide. The preparation of the hydrated bromide used indicated by such analysis the presence of 0.2% of the monobromide. Samples of different origin were used in different runs and the heat quantities showed good agreement among themselves.

Results and Calculations

The results are shown in Table I. Specific heats for the bromide solutions were taken from the work of Cobb and Gilbert.[3] The specific heat of solutions of the sulfate is not found in the literature, hence it has been determined over a limited concentration range by the same method (3) and is given in Table II. From the values of the total molal heat of solution ΔH in Column 4 of Table I,

TABLE I

HEATS OF SOLUTION AT 25° (IN 15° CAL.)

The molality of the dibromide is expressed in every case as moles of anhydrous salt in 1000 g. of water in the resulting solution.

Molality		Heat absorbed per mole of salt dissolved	Total molal heat of solution m_2
Initial m_1	Final m_2		
	Hydrazonium Sulfate		
0.00	0.0576	8132	8132
.00	.0579	8134	8134
.00	.0567	8171	8171
	Hydrazonium Dibromide Dihydrate		
0.00	0.1327	11106	11106
.00	.1322	11130	11130
	Hydrazonium Dibromide, Anhydrous		
0.00	0.1314	4862	4862
.00	.1326	4866	4866
.00	.1874	4840	4840
.1314	.2455	4718	4794
.1874	.2768	4686	4790
.1326	.3181	4671	4755
.2455	.4566	4493	4655
.3181	.5111	4336	4600
.4556	.6641	4164	4502
.6641	.8387	3882	4372

TABLE II

SPECIFIC HEAT OF AQUEOUS HYDRAZONIUM SULFATE AT 25°

Molality	Sp. ht. in 15° cal. per g.
0.00	0.9979
.0476	.9930
.0795	.9889
.0856	.9891
.1058	.9852

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[1] Gilbert and Cobb, THIS JOURNAL, **57**, 39 (1935).

[2] R. Bach, *Z. physik. Chem.*, **9**, 241 (1892).

[3] Cobb and Gilbert, THIS JOURNAL, **57**, 35 (1935).

the partial molal heat of solution of the solute and the relative partial molal heat content of the solvent were computed for the bromide solutions by the methods of the previous paper.[1] They are shown in Table III.

TABLE III

PARTIAL MOLAL HEATS OF SOLUTION OF SOLVENT AND SOLUTE AT 25° IN 15° CAL.

Molality	$\overline{H}_2 - H_2(\text{s})$	$\overline{H}_1 - \overline{H}_1^0$
Hydrazonium Dibromide		
0.1	4849	0.0427
.2	4712	.4268
.3	4571	1.059
.5	4265	3.216
.8	3870	7.739

Discussion

The low solubility of the sulfate limited this study to small concentrations. The most disturbing aspect of the problem, however, was the extreme slowness with which this salt dissolved even at concentrations considerably removed from saturation. The runs on the sulfate took from ninety to one hundred twenty minutes for completion. This resulted in a relatively large correction for heat of stirring, and required the use of small samples (5 g.) with attendant small temperature effects. For this reason the probable error in the heat of solution of the sulfate is larger than for any other salt in the series investigated.

Examination of the results obtained for the two series of chlorides and bromides (from this and the previous paper[1]), in which hydrazine functions, respectively, as a mono- and di-acid base, and comparison with other salts reveals some interesting correlations. In Table IV have been collected the differences in the molal integral heats of solution for a number of chlorides and bromides of the alkali and alkaline earth groups.[4] Inspection of this table of rounded values shows that salts of the monovalent hydrazonium ion $N_2H_5^+$ exhibit a behavior analogous to those of potassium, ammonium, rubidium and cesium, in that the bromide absorbs *more* heat than the chloride. In the hydrazonium salts containing two equivalents of acid, however, the bromide absorbs *less* heat than the chloride, a behavior similar to that of lithium, sodium, barium, strontium, and other hydrated cations. This difference in heat of solution, however, may be almost quantitatively accounted for by the difference in the heats of solution of the additional mole of halogen acid. The further similarity of the hydrated hydrazonium dibromide to the other bromides shown in the table is not so easily explained, but re-emphasizes[5] the similarity of the behavior of hydrazonium and sodium salts.

TABLE IV

COMPARISON OF MOLAL INTEGRAL HEATS OF SOLUTION: BROMIDES AND CHLORIDES OF THE ALKALI AND ALKALINE EARTH GROUPS, AND HYDRAZINE

Data for Li, Rb and Cs are given for 15°; Na, Ba, Sr, K and NH_4, 18°; hydrazine salts, 25°. Concentration in all cases except NH_4 is *ca.* 1 mole of salt to 400 or more moles of water; for NH_4, 1 to 200.

Element	$\Delta H(\text{Br}^-) - \Delta H(\text{Cl}^-)$	$\Delta H(\text{Br}^-\cdot 2H_2O) - \Delta H(\text{Br}^- \text{ Anhyd.})$
Li	−2900	(*ca.*) +12000
Na	−1100	+ 4900
Ba	−2900	+ 9160
Sr	−4880	+ 9825
$N_2H_6^{++}$	−1164	+ 6250
K	+ 680	
NH_4^+	+ 550	
Rb	+1500	
Cs	+2000	
$N_2H_5^+$	+1100	

Summary

New data are reported on the heats of solution in water at 25° of hydrazonium dibromide, anhydrous and hydrated, and of hydrazonium sulfate.

The partial molal heat of solution of the solute and the solvent have been computed for the bromide.

The specific heat capacity of hydrazonium sulfate solutions at 25° has been determined.

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(4) "International Critical Tables," Vol. V, p. 169 ff.; Lange, "Handbook of Chemistry," 1934, pp. 1017-1024, Handbook Publishing Co., Sandusky, Ohio.

(5) Christensen and Gilbert, THIS JOURNAL, **56**, 1897 (1934).