known about the actual species formed. Scholder[15] reports preparing well crystallized compounds like $Ba_2[Co(OH)_6]$ and $Na_2[Co(OH)_4]$. More recently Gordon and Schreyer[16] have studied spectrophotometrically the species of cobalt(II) in strongly alkaline solutions and report results indicating that a blue trihydroxocobalt(II) exists in solutions containing 3 to 12 *M* potassium hydroxide.

Some experiments were carried out in order to find out whether the blue complex of cobalt(II) is reducible at the dropping mercury electrode. The supporting electrolyte (10 *M* sodium hydroxide) was deaerated and then a few drops of a 2 *M* cobaltous sulfate solution were added to it. A pink to blue precipitate was at first formed, but after 15 minutes' stirring (nitrogen bubbling) a deep blue solution was obtained, containing about 2 millimolar of cobalt(II) as the hydroxo complex. Most of the precipitated cobaltous hydroxide remained undissolved. The reduction proceeded irreversibly, the half-wave potential being -1.54 v. *vs.* S.C.E.

The reduction of the hexamminecobalt(III) complex in 10 *M* sodium hydroxide was also studied. The first step comes at around -0.35 v. *vs.* S.C.E. and the second step has a half-wave potential of -1.54 v. *vs.* S.C.E. It seems obvious that the mechanism is similar to that described in the case of the chloro complex.

Whether the exchange here is complete or not cannot be said on the basis of this experiment.

Acknowledgment.—This investigation has been supported by the Office of Naval Research under Contract No. N6 ori-07136.

URBANA, ILLINOIS

[15] R. Scholder, *Z. angew. Chem.*, **46**, 509 (1933).

[16] S. Gordon and J. M. Schreyer, THIS JOURNAL, **74**, 3169 (1952).

[CONTRIBUTED FROM THE ROSS CHEMISTRY LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

The Thermodynamics of Aqueous 2-Propanol–Sulfuric Acid Solutions from Electromotive Force Measurements[1]

BY WILLIAM N. WHITTEN AND JAMES E. LAND

RECEIVED DECEMBER 10, 1952

Electromotive force measurements have been made at 5, 10, 15 and 20° with cells consisting of a hydrogen electrode and a mercury–mercurous sulfate electrode in aqueous 2-propanol–sulfuric acid solutions. The solutions contained 5 and 10% by weight 2-propanol and the acid molalities varied from 0.05 to 1.0. From these electromotive force values the mean ionic activity coefficients of the acid have been calculated. The relative partial molal heat contents of the sulfuric acid in these solutions have been computed for the temperature range 5 to 25°.

The mean ionic activity coefficients of sulfuric acid in aqueous 2-propanol solutions at 25° have been determined by Land and Crockford.[2]

The purpose of the investigation reported on in this paper was, first, to determine the mean ionic activity coefficients of sulfuric acid in the same solvent media at 5, 10, 15 and 20°. Then, these values and the mean ionic activity coefficients previously measured at 25° permitted the variation of the mean ionic activity coefficients with temperature to be found, so that the relative partial molal heat content of the sulfuric acid in aqueous 2-propanol mixtures could be calculated for the temperature range 5 to 25°.

The cell used in these studies was

$$H_2(g)/H_2SO_4(m),\ \text{2-propanol}\ (x\%),\ \text{water}\ (100 - x\%)/Hg_2SO_4(s)/Hg(l)$$

5 and 10% by weight aqueous solutions of 2-propanol were studied. The molalities of the sulfuric acid employed ranged from 0.05 to 1.0 molal. Readings below 0.05 molal and above 1.0 molal were not attempted for reasons previously reported.[2]

Experimental Procedure.—The methods of purification of chemicals, experimental techniques and equipment employed were the same as those used by Land and Crockford.[2] Density measurements were made on all solutions at 5, 10, 15 and 20°.

In order that all electromotive force measurements could be corrected to one atmosphere pressure of dry hydrogen, the vapor pressures of all solutions over the entire range of temperatures studied were determined by the method used by Crockford, Bailey and Land.[3] The vapor pressure results for solutions not exceeding one molal of sulfuric acid in 5 and 10% by weight 2-propanol–water solutions can be expressed by the equation

$$\text{v.p.} = \alpha - \beta(m)$$

in which α and β are constants. These constants are given in Table I.

TABLE I

CONSTANTS OF THE EQUATION V.P. $= \alpha - \beta(m)$

Temp., °C.	α		β	
	5% 2-propanol-water soln.	10% 2-propanol-water soln.	5% 2-propanol-water soln.	10% 2-propanol-water soln.
5	7.9	8.6	0.40	0.13
10	10.7	11.7	.31	.20
15	14.6	16.2	.51	.42
20	20.1	22.4	.71	.22

Data and Results.—Tables II and III give a summary of the mean ionic activity coefficients determined. The values of *E* recorded were ascertained from very large scale curves obtained by plotting the experimentally determined electromotive force values against the square root of the molality. The density values were also obtained

---

[1] Based partly upon William N. Whitten's M.S. thesis. Presented at the Southeastern Regional Meeting of the American Chemical Society, October 23–25, 1952.

[2] J. E. Land and H. D. Crockford, THIS JOURNAL, **72**, 1895 (1950).

[3] H. D. Crockford, W. Bailey and J. E. Land, *J. Alabama Acad. of Science*, **21**, 12 (1952).

TABLE II

MEAN IONIC ACTIVITY COEFFICIENTS OF SULFURIC ACID IN 5% 2-PROPANOL–WATER SOLUTION

	5°				10°			
Molality	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$
0.05	0.9947	0.7493	0.395	0.468	0.9944	0.7498	0.372	0.439
.10	0.9980	.7333	.309	.366	0.9977	.7335	.291	.343
.20	1.0046	.7170	.243	.288	1.0040	.7170	.229	.270
.30	1.0111	.7074	.211	.250	1.0103	.7073	.198	.234
.40	1.0174	.7005	.192	.228	1.0164	.7002	.181	.213
.50	1.0236	.6948	.180	.213	1.0225	.6944	.169	.200
.60	1.0297	.6900	.171	.203	1.0285	.6897	.161	.190
.70	1.0356	.6860	.165	.196	1.0344	.6855	.155	.182
.80	1.0417	.6823	.160	.189	1.0404	.6817	.150	.177
.90	1.0477	.6789	.156	.185	1.0462	.6782	.147	.173
1.00	1.0536	.6757	.153	.181	1.0519	.6750	.144	.170
		E^0 = 0.6249 v.				E^0 = 0.6210 v.		

	15°				20°			
Molality	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$
0.05	0.9939	0.7502	0.354	0.416	0.9929	0.7505	0.334	0.393
.10	0.9972	.7336	.275	.323	0.9961	.7337	.262	.309
.20	1.0033	.7169	.216	.254	1.0024	.7167	.204	.241
.30	1.0094	.7070	.188	.221	1.0084	.7068	.178	.209
.40	1.0154	.6998	.170	.201	1.0143	.6994	.161	.190
.50	1.0214	.6940	.160	.188	1.0203	.6934	.151	.177
.60	1.0273	.6891	.152	.178	1.0261	.6885	.144	.169
.70	1.0331	.6849	.146	.171	1.0318	.6842	.138	.162
.80	1.0390	.6811	.142	.167	1.0375	.6803	.134	.157
.90	1.0448	.6775	.138	.162	1.0431	.6768	.131	.154
1.00	1.0502	.6743	.135	.158	1.0488	.6735	.128	.150
		E^0 = 0.6171 v.				E^0 = 0.6132 v.		

TABLE III

MEAN IONIC ACTIVITY COEFFICIENTS OF SULFURIC ACID IN 10% 2-PROPANOL–WATER SOLUTION

	5°				10°			
Molality	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$
0.05	0.9885	0.7446	0.395	0.533	0.9879	0.7456	0.377	0.498
.10	.9917	.7287	.308	.416	.9911	.7293	.292	.386
.20	.9981	.7127	.240	.324	.9973	.7131	.227	.300
.30	1.0043	.7031	.209	.282	1.0034	.7034	.198	.262
.40	1.0105	.6962	.191	.258	1.0094	.6963	.179	.236
.50	1.0165	.6908	.178	.242	1.0154	.6906	.168	.221
.60	1.0224	.6861	.170	.229	1.0211	.6858	.159	.210
.70	1.0284	.6820	.162	.219	1.0270	.6816	.153	.202
.80	1.0342	.6782	.157	.212	1.0327	.6779	.150	.198
.90	1.0399	.6749	.153	.206	1.0383	.6745	.145	.192
1.00	1.0455	.6717	.149	.201	1.0437	.6714	.142	.188
		E^0 = 0.6202 v.				E^0 = 0.6169 v.		

	15°				20°			
Molality	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$	Density	E	$\gamma_\pm$	$\gamma_\pm{}^*$
0.05	0.9870	0.7461	0.358	0.463	0.9857	0.7467	0.343	0.437
.10	.9902	.7298	.278	.360	.9888	.7301	.266	.339
.20	.9962	.7133	.216	.280	.9949	.7129	.206	.262
.30	1.0023	.7034	.188	.243	1.0008	.7034	.178	.227
.40	1.0082	.6962	.170	.220	1.0068	.6962	.162	.206
.50	1.0141	.6905	.159	.206	1.0127	.6902	.152	.194
.60	1.0198	.6856	.152	.197	1.0184	.6853	.144	.183
.70	1.0255	.6813	.146	.189	1.0239	.6810	.139	.177
.80	1.0311	.6775	.141	.183	1.0294	.6771	.134	.171
.90	1.0367	.6740	.137	.177	1.0349	.6735	.131	.169
1.00	1.0422	.6709	.134	.174	1.0404	.6702	.128	.163
		E^0 = 0.6135 v.				E^0 = 0.6101 v.		

from large plots. The mean ionic activity coefficients were calculated from the equation

$$E = E^0 - 3RT/2F \ln (4^{1/3} m\gamma_\pm)$$

The calculations of the mean ionic activity coefficients, $\gamma_\pm$, were based upon a reference state of unit mean ionic activity coefficient for the acid at infinite dilution in the designated solvent under a pressure of one atmosphere and at the stated temperature. The mean ionic activity coefficients,

$\gamma^*_\pm$, were based upon a reference state of unit mean ionic activity coefficient of the acid at infinite dilution in pure water. For this latter value it was necessary to employ the standard molal potentials reported by Harned and Hamer.[4]

Since electromotive force measurements could not be made in concentrations below 0.05 molal, the usual extrapolation technique for determining the standard electrode potentials for cells containing these solutions could not be successfully employed. Instead the E^0 values quoted in Tables II and III were arrived at by the method used by Crockford and Wideman.[5]

Curves obtained by plotting the values of $\gamma_\pm$ and $\gamma^*_\pm$ against the square root of the molality show a similar shape to those obtained for sulfuric acid in pure water.

Plots of the ln $\gamma_\pm$ for each molality in both the 5 and 10% by weight 2-propanol-water solutions against the absolute temperature indicate a straight line function. Using the method of least squares, the slope, $\partial \ln \gamma_\pm/\partial T$, for each curve was determined. By means of the equation

$$\bar{L}_2 = -3RT^2(\partial \ln \gamma_\pm/\partial T)$$

the relative partial molal heat content of sulfuric acid has been calculated for each molality listed in Tables II and III over the temperature range 5 to 25°.

TABLE IV

THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF SULFURIC ACID IN 5% 2-PROPANOL–WATER SOLUTION RELATIVE TO INFINITE DILUTION

$m(H_2SO_4)$	$\bar{L}_2(5°)$	$\bar{L}_2(10°)$	$\bar{L}_2(15°)$	$\bar{L}_2(20°)$	$\bar{L}_2(25°)$
0.05	4738	4910	5085	5263	5444
.10	5105	5290	5479	5671	5866
.20	5322	5515	5712	5911	6115
.30	5438	5636	5837	6041	6249
.40	5500	5700	5903	6110	6320
.50	5545	5746	5951	6160	6372
.60	5557	5758	5964	6172	6385
.70	5565	5767	5972	6182	6394
.80	5577	5779	5985	6195	6408
.90	5585	5788	5994	6204	6417
1.00	5690	5897	6107	6321	6539

TABLE V

THE RELATIVE PARTIAL MOLAL HEAT CONTENTS OF SULFURIC ACID IN 10% 2-PROPANOL–WATER SOLUTIONS RELATIVE TO INFINITE DILUTION

$m(H_2SO_4)$	$\bar{L}_2(5°)$	$\bar{L}_2(10°)$	$\bar{L}_2(15°)$	$\bar{L}_2(20°)$	$\bar{L}_2(25°)$
0.05	4109	4258	4410	4564	4722
.10	4393	4552	4715	4880	5048
.20	4720	4891	5065	5243	5423
.30	4892	5070	5251	5438	5622
.40	4983	5163	5348	5535	5725
.50	5030	5213	5399	5588	5780
.60	5062	5245	5432	5622	5816
.70	5082	5267	5455	5646	5840
.80	5091	5275	5464	5655	5850
.90	5113	5298	5487	5680	5875
1.00	5156	5344	5534	5728	5925

The values of $\bar{L}_2$, as read from the best smooth curve on a large scale plot of the calculated $\bar{L}_2$ values against $m^{1/2}$, are reported in Tables IV and V. Isothermal curves obtained by plotting $\bar{L}_2$ against the square root of the molality show a similar shape to those reported in the literature for sulfuric acid in pure water, but the respective values for $\bar{L}_2$ are greater over the concentration range studied in the 2-propanol–water solutions as compared to pure water as the solvent.

AUBURN, ALABAMA

---

[4] H. S. Harned and W. J. Hamer, THIS JOURNAL, **57**, 27 (1935).

[5] H. D. Crockford and S. A. Wideman, *J. Phys. Chem.*, **50**, 418 (1946).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BARNARD COLLEGE, COLUMBIA UNIVERSITY]

The Ionization Constants of Taurine and its Activity Coefficient in Hydrochloric Acid Solutions from Electromotive Force Measurements

BY EDWARD J. KING

RECEIVED NOVEMBER 25, 1952

The electromotive forces of cells with hydrogen and silver–silver chloride electrodes that contained either taurine–sodium taurinate–sodium chloride buffers (cell I) or taurine–hydrochloric acid mixtures (cell II) have been measured at 5° intervals from 10 to 50°. From the data for cell I the thermodynamic ionization constant, K_2, associated with the ionization of the ammonium group has been calculated. The values fit the equation $-\log K_2 = (2458.49/T) - 0.0997 + 0.0030689T$ and from this have been derived the changes in free energy, enthalpy, entropy and heat capacity associated with the ionization. The measurements on cell II were used to find the effect of taurine upon the activity coefficient of hydrochloric acid and the activity coefficient of taurine (γ_1) in the hydrochloric acid solutions. The limiting slope for the variation of log γ_1 with the concentration of hydrochloric acid is used in connection with a theory of Kirkwood to calculate the dipole moment of taurine in solution. For either a spherical or an ellipsoidal model of the taurine molecule the calculated dipole moment was 18 ± 1 which is of the right order of magnitude. The salting-out effect cannot be neglected in discussing the behavior of taurine in hydrochloric acid solutions. The measurements on cell II were also used in an attempt to determine the ionization constant (K_1) of the sulfonic acid group, but it was found to be only possible to state that K_1 is larger than one.

In recent papers values of the ionization constants of sulfamic[1,2] and sulfanilic[3] acids have been reported. The electrolytic behavior of taurine, the aminosulfonic acid analogous to β-alanine, is the subject of the present communication. Its low ionization constant (8.69×10^{-10} at 25°), its high dielectric increment (41),[4] and the absence from its infrared spectrum of the absorption band near 1.04 μ

---

[1] E. G. Taylor, R. P. Desch and A. J. Catotti, THIS JOURNAL, **73**, 74 (1951).

[2] E. J. King and G. W. King, *ibid.*, **74**, 1212 (1952).

[3] R. O. MacLaren and D. F. Swinehart, *ibid.*, **73**, 1822 (1951).

[4] G. DeVoto, *Gazz. chim. ital.*, **61**, 897 (1931).