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The Activity Coefficients and Complex of Mercury(I) Sulfate in Sulfuric Acid Solutions at 25°[1]

BY SHIRLEY A. BROWN AND JAMES E. LAND

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The solubility of mercury(I) sulfate in sulfuric acid solutions of various molalities was measured at 25°. By employing the values for the ratio of the concentration of hydrogen sulfate ions to the concentration of sulfate ions in these sulfuric acid solutions as given from Raman spectra, the ionic strengths of the mercury(I) sulfate, sulfuric acid solutions were calculated. From a plot of the reciprocal of the mean molality of the mercury(I) and sulfate ions *vs.* the cube root of the ionic strength, an extrapolation gave the theoretical solubility product constant for the mercury(I) sulfate in water. This constant then was used to compute the mean ionic activity coefficients of the mercury(I) sulfate in sulfuric acid solutions with concentrations between 0.002 and 2 *m*. A mechanism for the formation of the species $H[Hg_2(SO_4)(HSO_4)]$ was postulated and proof of its existence in solution advanced.

The use of mercury(I) sulfate in the preparation of standard e.m.f. cells has prompted many studies on its solubility in water and sulfuric acid solutions. A most complete and conclusive article on this topic is that of Craig, *et al.*,[2] who reported on the solubility of mercury(I) sulfate in sulfuric acid solutions from 0.002 to 3.5 *c* at 0 and 28°, and also they showed that a linear interpolation of their results to 25° agreed very closely with those reported by Hulett.[3]

Our interest in the mean ionic activity coefficients of mercury(I) sulfate grew out of an attempt to overcome certain difficulties in the calculation of the E^0 for the H_2, H_2SO_4, solvent, Hg_2SO_4, Hg e.m.f. cell used in determining the mean ionic activity coefficients of sulfuric acid at low molalities in mixed solvents.[4]

Not being able to compute the practical activity coefficients of mercury(I) sulfate in sulfuric acid solutions from the solubility results given in the literature, since they were recorded in molarities and density values were not reported, we performed enough solubility measurements over the range of acid molalities reported to give a relationship between concentration and density at 25°. With such results and those in the literature the mean ionic activity coefficients of mercury(I) sulfate in sulfuric acid were calculated and also it was possible to postulate the presence of a soluble mercury complex.

Experimental

Solid mercury(I) sulfate, prepared by the method of Hulett,[5] was added in excess to the sulfuric acid solutions contained in brown, ground glass stoppered bottles. The sealed bottles were agitated mechanically in a constant temperature bath maintained at 25 ± 0.02° for 3–4 days. After agitation the solutions were allowed to stand in the bath until clear, a sample removed by suction into a special pycnometer (previously described[6]) for the density determination, then analyzed for Hg and sulfuric acid using techniques described in reference 2.

Results and Discussion

Over the range of concentrations of sulfuric acid studied it was found that the density at 25° of the mercury(I) sulfate–sulfuric acid solutions could be represented as a function of acid molarity by the equation

$$d = 0.9975 + 0.0624c_{(H_2SO_4)} + 1.0918 \times 10^{-3}c_{(H_2SO_4)}$$

The molalities of the dissolved mercury(I) sulfate determined agreed within experimental error with those computed from the results of Craig, *et al.*,[2] using the above density, concentration relationship.

From a large scale plot of the molality of the mercury(I) sulfate (using both our measured values and those computed from reference 2) against the log of the molality of the sulfuric acid,

TABLE I

THE SOLUBILITIES, THE RECIPROCAL OF THE MEAN IONIC MOLALITIES, AND THE MEAN IONIC ACTIVITY COEFFICIENTS OF MERCURY(I) SULFATE AND THE MOLALITIES OF THE SULFATE ION AND THE FACTOR FOR ITS DETERMINATION IN SULFURIC ACID SOLUTIONS OF VARIOUS MOLALITIES

m of H_2SO_4	$m \times 10^4$ of Hg_2SO_4	γ_R	*m* of $(SO_4)^-$	$1/m_\pm$	μ	$\gamma_\pm$
0.002	11.120	0.972	0.002	820.6	0.007	0.677
.003	10.158	.956	.002	679.8	.009	.561
.004	9.455	.942	.003	634.2	.011	.523
.005	8.923	.926	.003	601.2	.013	.496
.006	8.608	.912	.004	576.1	.015	.475
.007	8.386	.896	.004	553.0	.016	.456
.008	8.262	.882	.004	536.8	.018	.443
.009	8.141	.866	.005	516.7	.020	.426
.010	8.068	.852	.005	502.9	.021	.415
.020	7.574	.710	.008	416.8	.037	.344
.030	7.450	.582	.010	362.8	.052	.299
.040	7.557	.474	.013	320.3	.066	.264
.050	7.641	.380	.016	284.2	.082	.234
.060	7.746	.300	.020	254.1	.100	.210
.070	7.854	.250	.024	231.8	.117	.191
.080	7.968	.215	.027	214.4	.135	.177
.090	8.041	.189	.031	200.6	.152	.166
.100	8.119	.170	.034	189.2	.169	.156
.200	8.867	.108	.060	137.2	.320	.113
.300	9.373	.078	.086	111.6	.471	.092
.400	9.783	.054	.120	92.4	.640	.076
.500	10.062	.035	.170	76.6	.839	.063
.600	10.291	.032	.198	70.0	.997	.058
.700	10.463	.029	.216.	66.6	1.132	.055
.800	10.555	.027	.240	62.9	1.279	.052
.900	10.573	.025	.265	59.8	1.430	.049
1.000	10.549	.019	.320	54.4	1.640	.045
1.500	9.966	.014	.467	46.4	2.434	.038
2.000	9.091	.010	.631	41.8	3.262	.034

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[1] Presented at the Southwide Chemical Conference of The American Chemical Society, December 6–8, 1956.

[2] D. N. Craig, G. W. Vinal and F. E. Vinal, *J. Research Natl. Bur. Standards*, **17**, 709 (1936). This reference contains a bibliography and a critical evaluation of all articles published on this subject to 1936.

[3] G. A. Hulett, *Trans. Am. Electrochem. Soc.*, **6**, 109 (1904).

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

[5] G. A. Hulett, *Phys. Rev.*, **32**, 257 (1911).

[6] S. A. Brown and J. E. Land, *J. Chem. Educ.*, **33**, 72 (1956).

the values recorded in the accompanying table were taken.

To calculate the mean ionic molality of the mercury(I) sulfate, the needed molality of the sulfate ion was computed from the mass law equation for the dissociation of the HSO_4^- ion

$$K_{HSO_4^-} = \frac{(m_{H^+})(m_{SO_4^{=}})}{(m_{HSO_4^-})} \times \gamma_R$$

Values for the factor γ_R listed in the accompanying table were taken from a large scale plot of the values reported by Smith.[7]

The concentration of the HSO_4^- ion can be taken as the difference between the molality of the sulfuric acid and the $SO_4^{=}$ ion since Smith's work demonstrated no undissociated sulfuric acid to be present in the range reported here. The value used for $K_{HSO_4^-}$ was 0.0120.[8]

The mean ionic activity coefficients listed in the accompanying table were determined from the equation $\gamma_\pm = (1/m_\pm)K^{1/3}$, where $m_\pm$ is the mean ionic molality and K is the hypothetical thermodynamic solubility product constant for the mercury(I) sulfate. $K^{1/3}$ was determined by plotting $1/m_\pm$ *vs.* the cube root of the ionic strength and extrapolating to zero ionic strength. The value found for K was 6.81×10^{-7}.

The behavior of $\gamma_\pm$ with changing ionic strength is illustrated in Fig. 1.

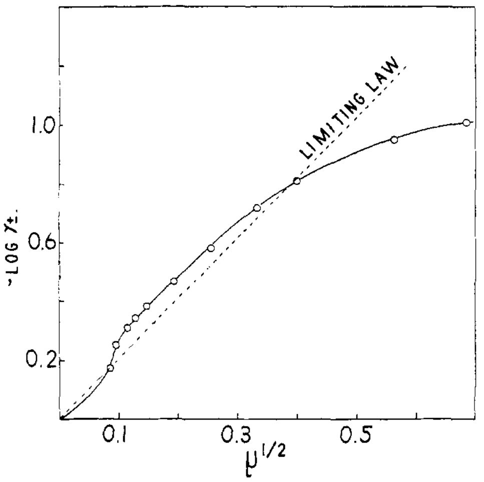

Fig. 1.

The shape of the solubility curve of mercury(I) sulfate in sulfuric acid solution indicated the formation of a soluble complex. Eppley[9] suggested that between 0 and 0.15 *c* sulfuric acid a basic, normal and acid species of Hg_2SO_4 existed. Craig, *et al.*,[2] postulated the formation of the compound $HgHSO_4$ to account for the increased solubility of the mercury(I) sulfate. Kendall and Davidson[10] reported the formation of the unstable acid salt $Hg_2SO_4 \cdot H_2SO_4$ from the analysis of the solid plase in contact with solutions of mercury(I) sulfate in 100% sulfuric acid.

Since the increase in solubility of the mercury(I) sulfate coincides with the increase in the HSO_4^- ion concentration, it was reasoned that such an equilibrium as this is possible

$$Hg_2SO_4 + n(HSO_4^-) \rightleftharpoons [Hg_2(SO_4)(HSO_4)_n]^{n-}$$

Taking the logarithm of both sides of the mass law equation for this equilibrium and rearranging gives

$$\log a_{[Hg_2(SO_4)(HSO_4)_n]^{n-}} = n \log a_{HSO_4^-} + \log K$$

thereby indicating that a plot of the $\log a_{[Hg_2(SO_4)(HSO_4)_n]^{n-}}$ *vs.* $\log a_{HSO_4^-}$ should produce a straight line of slope n and intercept equal to $\log K$, if such an equilibrium is the case.

The concentration of the soluble mercury complex was taken as the difference between the molality of the mercury(I) sulfate at all values of $m_{H_2SO_4}$ between 0.06 and 0.4 and that at $m_{H_2SO_4} = 0.03$, since the mercury(I) sulfate concentration at this latter molality may be considered to be the maximum possible concentration of the Hg_2SO_4 species in sulfuric acid solutions more concentrated than 0.03 *m*. A plot of $-\log m_{[Hg_2(SO_4)(HSO_4)_n]^{n-}}$ *vs.* $-\log m_{HSO_4^-}$, shown in Fig. 2,[11] gave

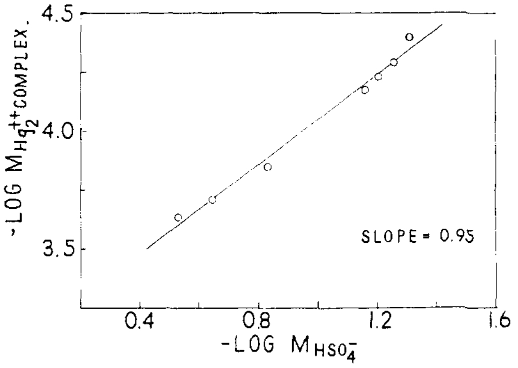

Fig. 2.

a series of points that fall close to a straight line with a slope of 0.95, thereby indicating the probable complex ion to be $[Hg_2(SO_4)(HSO_4)]^-$.

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(7) H. M. Smith, Ph.D. thesis, University of Chicago, 1949.

(8) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 430.

(9) M. Eppley, *Trans. Am. Electrochem. Soc.*, **53**, 172 (1928).

(10) J. Kendall and A. W. Davidson, THIS JOURNAL, **43**, 979 (1921).

(11) For an explanation of the use of concentration rather than activity terms, *cf.* A. B. Garrett, M. V. Noble and S. Miller, *J. Chem. Educ.*, **19**, 486 (1942).