3. Manganese may play a role in plankton growth as the element was found in the ash of these organisms, amounting to 0.07% of the ash weight. Furthermore, waters rich in plankton showed less dissolved manganese.

4. Manganese was found in various muds collected from the sea bottom, the manganese content varying from 0.05 to 0.30% of the dried sample.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE CONNECTICUT STATE COLLEGE]

Measurement of the Interfacial Tension at a Mercury–Mercurous Sulfate Solution Interface by the Drop Weight Method

BY KENNETH E. GLIDDEN

Introduction

The purpose of this investigation was to measure the interfacial tension at a mercury–mercurous sulfate solution interface by the drop weight method. The drop weight technique developed by Harkins and co-workers is particularly advantageous for such an investigation, and it is hoped that the measurements described in this paper will be of use in clarifying the question of mercurous ion adsorption at a mercury surface.[1]

Patrick measured the interfacial tension of mercury against aqueous solutions of mercurous sulfate and other substances.[2] In the case of mercurous sulfate, his values of interfacial tension are of the same order of magnitude as those reported in this paper, but it is doubtful whether his technique permitted equilibrium to be attained in the boundary region between mercury and solution, due to the rapid formation of mercury surface. The investigations of Harkins and others have demonstrated the necessity of slow drop formation, especially at the moment of rupture of the hanging drop from the dropping tip.

Apparatus

The drop weight apparatus was of the type developed by Harkins and Brown.[1] With the exception of a short length of 3-cm. tubing to act as a mercury reservoir, the apparatus was constructed of Pyrex capillary having a bore approximately 1.5 mm. in diameter. Since mercury does not wet glass, the drops fall from the bore of the capillary, and it is essential to have this portion of the tip uniform. By grinding the tip as recommended by Harkins, a tip free from cracks and jagged edges may be obtained. The radius of the tip was determined by measuring several diameters of the bore with a calibrated micrometer eyepiece in a microscope, and was found to be 0.0783 cm.

The solution under investigation was contained in a small weighing bottle, air and water being excluded by means of a tight-fitting rubber stopper. The entire apparatus was clamped in a frame, and suspended in a thermostat maintained at 20 ± 0.1°.

To control the speed of formation of the mercury drops, a U-tube of 3-cm. tubing approximately 50 cm. high was constructed. This was filled with mercury to about half its height, and one end connected to a suction pump and the atmosphere by means of a two-way stopcock. After partial evacuation of this end of the U-tube, the open end was connected to the open end of the drop weight apparatus. By turning the two-way stopcock, the pressure exerted on the mercury in the reservoir of the drop weight apparatus may be equal to or greater than atmospheric, thus regulating the speed of formation of the drops.

In order to control further the rate of drop formation, a portion of the capillary between the reservoir and tip must be constricted. In actual practice, it was more convenient to use several comparatively large constrictions rather than one fine one, since the fine constrictions are easily clogged by small dust particles.

Experimental Procedure

The drop weight apparatus was thoroughly cleaned with warm cleaning mixture, steamed for one-half hour, and dried. The tube was then filled by suction with carefully purified mercury until the level in the reservoir was approximately 2 cm. above the ground dropping tip. A solution of mercurous sulfate of known concentration was then placed in the weighing bottle, and the apparatus immersed in the thermostat, fifteen minutes to one-half hour being allowed for attainment of temperature equilibrium.

The mercurous sulfate solutions were prepared by saturating distilled water or *N*/40 sulfuric acid solution with C. P. mercurous sulfate in the presence of mercury to prevent the formation of mercuric salts. These saturated solutions were analyzed by electrolysis, and solutions of lower concentration obtained by dilution.

The following procedure was used in all determinations of the drop weight: the partially evacuated side of the mercury-filled U-tube was opened to the atmosphere, thus building up a pressure on the reservoir end of the drop weight apparatus. In this way, approximately 90% of the drop may be formed in forty-five seconds to one min-

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[1] Harkins and Brown, THIS JOURNAL, (a) **38**, 246 (1916); (b) **41**, 499 (1919).

[2] Patrick, *Z. physik. Chem.*, **86**, 545 (1914).

ute. Turning the stopcock to vacuum reduces the pressure, and the speed of formation is decreased to a very small value in a short time. The remainder of the drop is allowed to form under the influence of gravity. The average time for the formation of one drop varied from three to four minutes.

Ten to twenty drops were collected according to the above procedure. The apparatus was then removed from the thermostat, the mercury and solution poured on a filter paper, washed with distilled water, dried with acetone, and finally weighed to the nearest 0.2 mg.

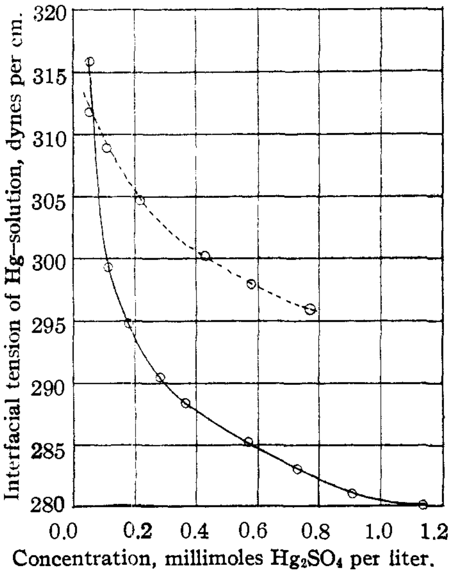

Fig. 1.—Interfacial tension–concentration curves: ----- Hg_2SO_4 in $N/40$ H_2SO_4; —— Hg_2SO_4 in distilled water.

Experimental Results.—Table I shows the data obtained with aqueous mercurous sulfate solutions. The corresponding data for $N/40$ sulfuric acid solutions are shown in Table II.

The interfacial tension mercury–solution was calculated from the equation

$$\sigma = \frac{(m - m')g}{2\pi r\Phi}$$

where σ is the interfacial tension in dynes per cm., m the weight of a drop in air, m' the weight of an equal volume of solution, r the radius of the capillary bore, g the gravity constant and Φ a factor calculated by Harkins and Brown.[1b] Knowing r and $V^{1/3}$, the cube root of the volume of the drop, Φ may be read from the curve or interpolated from the table obtained by Harkins and Brown.

TABLE I

MERCUROUS SULFATE IN DISTILLED WATER

Concn., millimoles/liter	−log concn.	m	$m - m'$	Φ	σ
1.140	−0.057	0.1036	0.0960	0.6836	280.0
0.912	+ .040	.1041	.0964	.6839	281.1
.730	.137	.1048	.0972	.6845	283.1
.570	.244	.1055	.0981	.6847	285.3
.365	.437	.1070	.0991	.6853	288.3
.285	.545	.1078	.0999	.6957	290.5
.182	.740	.1096	.1015	.6866	294.8
.114	.943	.1115	.1032	.6874	299.3
.057	1.244	.1180	.1093	.6898	316.0
.000	..	.1416	.1312	.6982	374.4

TABLE II

MERCUROUS SULFATE IN $N/40$ SULFURIC ACID

Concn., millimoles/liter	−log concn.	m	$m - m'$	Φ	σ
0.770	0.114	0.1101	0.1020	0.6869	296.0
.578	.238	.1108	.1026	.6872	298.0
.430	.367	.1117	.1036	.6874	300.2
.215	.668	.1135	.1051	.6879	304.7
.107	.970	.1152	.1068	.6890	309.0
.054	1.270	.1163	.1078	.6897	311.7
.000	..	.1202	.1114	.6912	321.4

The interfacial tension–concentration curves are shown in Fig. 1, and the interfacial tension–log c curves in Fig. 2.

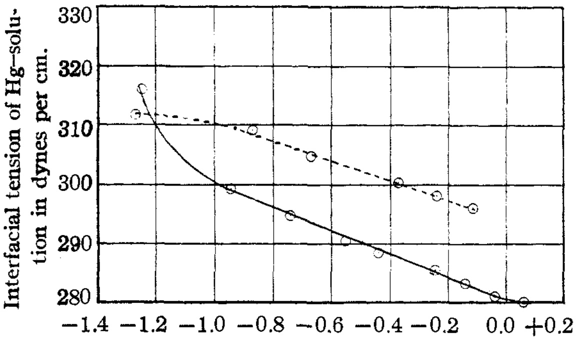

Fig. 2.—Interfacial tension–log c curves: ----- Hg_2SO_4 in $N/40$ H_2SO_4; —— Hg_2SO_4 in distilled H_2O.

Summary

1. The interfacial tension at a mercury–mercurous sulfate solution interface has been measured by the drop weight method.

2. The interfacial tension is a linear function of the logarithm of concentration down to a mercurous sulfate solution concentration of approximately 0.10 millimole per liter.

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