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The Hammett Acidity Function for Some Super Acid Systems. I. The Systems H_2SO_4–SO_3, H_2SO_4–HSO_3F, H_2SO_4–HSO_3Cl, and H_2SO_4–$HB(HSO_4)_4$

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Abstract: Using a set of aromatic nitro compound indicators, the Hammett acidity function, H_0, has been determined for the systems H_2SO_4–SO_3 (up to a composition of 75 mol % SO_3), H_2SO_4–HSO_3F, H_2SO_4–HSO_3Cl, and H_2SO_4–$HB(HSO_4)_4$.

The Hammett acidity function, H_0, first developed by Hammett and his coworkers[1] in the 1930's has been extensively used as a measure of the acidity of highly acidic media, in particular concentrated aqueous solutions of strong acids. A number of workers have since revised and extended Hammett's original measurements and a useful body of data has been accummulated, particularly for aqueous solutions of many of the common acids.[2] There has, however, been little work on the determination of the acidity of any highly acidic nonaqueous systems. In their original work Hammett and Deyrup made measurements on the H_2SO_4–H_2O system up to the composition of 100% H_2SO_4. These measurements were later extended by Brand[3,4] into the oleum region. The only other highly acidic nonaqueous system that has been studied is the H_2SO_4–HSO_3Cl system for which H_0 values were determined by Palm.[5] More recently, Jorgenson and Hartter[6] have pointed out that Hammett and Deyrup did not use a consistent set of indicators that overlapped with each other in a reliable manner. They therefore redetermined H_0 values for the H_2SO_4–H_2O system using a set of indicators which consisted only of primary anilines. Their measurements extended almost, but not quite, up to 100% H_2SO_4 and they have been accepted as the most reliable data for the H_2SO_4–H_2O system. Recently Johnson, Katritsky, and Shapiro[7] have published the results of a very careful study of the temperature dependence of H_0 for the system H_2SO_4–H_2O. Their results for 25° are in substantial agreement with Jorgenson and Hartter's data for room temperature. More recently Tickle and coworkers[8] published their temperature study of H_0 values for the H_2SO_4–H_2O system over a more limited temperature range. Their results show the same temperature dependence as found by Johnson, *et al.*,[7] but differ somewhat from Jorgenson and Hartter's room temperature measurements.

The work of Jorgenson and Hartter formed the basis for the present work, the object of which was to extend the range of acidity function measurements into the super acid region, *i.e.*, into the region of acidities greater than that of 100% H_2SO_4. In this paper we describe the results of our extension of the earlier data for the H_2O–H_2SO_4 system up to 100% H_2SO_4 and into the oleum region as well as the results of our measurements of the acidity of the H_2SO_4–$HB(HSO_4)_4$, H_2SO_4–HSO_3F, and H_2SO_4–HSO_3Cl systems. Subsequent papers will report the results of studies of the HSO_3F–SbF_5, HSO_3F–SbF_5–SO_3, and other super acid systems.[9]

It is difficult to find additional primary aniline indicators that are weaker bases than the weakest base used in previous studies of the H_2O–H_2SO_4 system, namely 2,4,6-trinitroaniline, and it was therefore necessary to choose another type of indicator. Following the earlier work of Brand[3,4] a series of substituted aromatic nitro compounds was chosen as these cover a useful range of acidity. The data obtained in this way probably do not have the same significance as the primary aniline data as it is less likely that the activity coefficient ratio $(f_C f_{BH^+}/f_{CH^+} f_B$, where B is a primary aniline (in this case 2,4,6-trinitroaniline) and C is an aromatic nitro compound (in this case *p*-nitrotoluene) will have the required value of unity than it has for two aniline bases. There is therefore some uncertainty associated with the overlap of the acidity range based on nitro compound indicators with the previously studied acidity range based on primary aniline indicators. However, as we will show, the overlap between these two indicators does in fact seem to be quite satisfactory. In any case, as all our measurements in super acid media have been carried out with the same set of nitro compound indicators it is felt that they constitute a self-consistent set of data and that they at least give relative values of the acidity of various super acid media.

Results and Discussion

The indicators used were 2,4,6-trinitroaniline, *p*-nitrotoluene, *m*-nitrotoluene, *p*-nitrofluorobenzene, *p*-

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Table I. Ionization Ratios for the H_2O–H_2SO_4–SO_3 System

Wt % H_2SO_4	Mol % H_2O	Log I	Wt % H_2SO_4	Mol % H_2O	Log I
2,4,6-Trinitroaniline			*m*-Nitrotoluene		
90.79	35.58	0.82	99.0	5.21	1.05
91.14	34.61	0.77	99.2	4.20	1.02
92.38	30.99	0.64	99.4	3.18	0.95
92.72	30.02	0.59	99.6	2.14	0.84
94.25	24.93	0.29	99.8	1.08	0.55
96.25	17.50	0.07	99.9	0.54	0.34
96.81	15.21	−0.08	100.0	Mol % SO_3	−0.04
97.93	10.32	−0.32	100.1	0.54	−0.17
98.18	9.16	−0.39	100.2	1.09	−0.31
98.39	8.18	−0.47	100.4	2.17	−0.43
98.66	6.89	−0.55	100.6	3.25	−0.57
99.31	3.64	−0.86	100.8	4.32	−0.68
p-Nitrotoluene			101.0	5.39	−0.72
96.41	16.86	1.34	Nitrobenzene		
96.81	15.21	1.14	99.80	1.08	0.88
97.76	11.09	1.06	99.84	0.87	0.89
98.20	9.07	0.84	99.90	0.54	0.55
98.60	7.17	0.73	99.94	0.33	0.53
98.79	6.25	0.70	99.94	0.33	0.25
98.95	5.46	0.57	100.00	Mol % SO_3	0.14
99.19	4.26	0.42	100.1	0.54	−0.02
99.38	3.28	0.31	100.2	1.09	−0.14
99.45	2.92	0.33	100.3	1.65	−0.23
99.60	2.14	0.15	100.4	2.17	−0.31
99.75	1.35	0.04	100.6	3.24	−0.45
99.95	0.27	−0.48	100.8	4.32	−0.56
100.00	Mol % SO_3	−0.67	101.0	5.39	−0.64
100.03	0.16	−0.75	101.5	8.04	−0.78
100.38	2.06	−1.05	102.0	10.67	−0.89
100.76	4.10	−1.26	103.0	15.85	−1.12
100.90	4.85	−1.29			

Mol % SO_3	Log I	Mol % SO_3	Log I
p-Nitrofluorobenzene			
1.0	0.19	12.0	−0.69
2.0	0.00	14.0	−0.78
3.0	−0.12	16.0	−0.87
4.0	−0.22	18.0	−0.93
5.0	−0.30	20.0	−1.02
6.0	−0.38	22.5	−1.11
7.0	−0.44	25.0	−1.20
8.0	−0.50	27.5	−1.26
9.0	−0.55	30.0	−1.33
10.0	−0.60		

Mol % SO_3	Log I	Mol % SO_3	Log I	Mol % SO_3	Log I
p-Nitro-		27.5	−0.01	25.0	−0.43
chlorobenzene		30.0	−0.08	27.5	−0.52
1.0	0.36	32.5	−0.16	30.0	−0.61
2.0	0.21	35.0	−0.24	32.5	−0.71
3.0	0.11	37.5	−0.30	35.0	−0.80
4.0	0.03	40.0	−0.38	37.5	−0.88
5.0	−0.04	42.5	−0.46	40.0	−0.97
6.0	−0.10	45.0	−0.55	2,4-Dinitrofluorobenzene	
7.0	−0.16	47.5	−0.63	25.0	0.65
8.0	−0.20	50.0	−0.70	27.5	0.56
9.0	−0.25	52.5	−0.78	30.0	0.48
10.0	−0.30	55.0	−0.86	32.5	0.40
12.0	−0.38	57.5	−0.83	35.0	0.32
14.0	−0.45	60.0	−1.00	37.5	0.24
16.0	−0.51	62.5	−1.04	40.0	0.16
18.0	−0.57	65.0	−1.09	42.5	0.07
20.0	−0.62	*m*-Nitrochlorobenzene		45.0	−0.03
22.5	−0.69	6.0	0.34	47.5	−0.17
25.0	0.76	7.0	0.28	50.0	−0.33
27.5	−0.84	8.0	0.24	52.5	−0.47
30.0	−0.92	9.0	0.19	55.0	−0.56
32.5	−0.99	10.0	0.15	57.5	−0.65
35.0	−1.06	12.0	0.06	60.0	−0.73
37.5	−1.14	14.0	−0.00	62.5	−0.79
40.0	−1.21	16.0	−0.08	65.0	−0.84
2,4-Dinitrotoluene		18.0	−0.16	67.5	−0.88
20.0	0.26	20.0	−0.24	70.0	−0.90
22.5	0.17	22.5	−0.34	72.5	−0.92
25.0	0.08			75.0	−0.94

Table II. Ionization Ratios

H_2SO_4–$HB(HSO_4)_4$					
Mol % HB-$(HSO_4)_4$	Log I	Mol % HB-$(HSO_4)_4$	Log I	Mol % HB-$(HSO_4)_4$	Log I
		p-Nitro-			
m-Nitrotoluene		chlorobenzene		2,4-Dinitrotoluene	
1.56	−0.15	1.56	−0.07	2.21	1.09
		2.21	−0.18	10.06	0.62
Nitrobenzene				27.0	0.19
1.56	−0.36			32.0	0.10
2.21	−0.42				
10.06	−1.22				

H_2SO_4–HSO_3F					
Mol % HSO_3F	Log I	Mol % HSO_3F	Log I	Mol % HSO_3F	Log I
p-Nitro-		*m*-Nitro-		2,4-Di-	
chlorobenzene		chlorobenzene		nitrotoluene	
5.0	0.52	5.0	0.84	45.0	0.80
10.0	0.33	10.0	0.71	50.0	0.73
15.0	0.20	15.0	0.62	55.0	0.67
20.0	0.09	20.0	0.54	60.0	0.60
25.0	0.01	25.0	0.47	65.5	0.53
30.0	−0.06	30.0	0.39	70.0	0.46
35.0	−0.12	35.0	0.32	75.0	0.39
40.0	−0.18	40.0	0.25	80.0	0.30
45.0	−0.24	45.0	0.18	85.0	0.19
50.0	−0.30	50.0	0.11	90.0	0.05
55.0	−0.36	55.0	0.04	95.0	−0.18
60.0	−0.42	60.0	−0.02	99.0	−0.51
65.0	−0.50	65.0	−0.10	2,4-Dinitrofluorobenzene	
70.0	−0.57	70.0	−0.17	80.0	1.08
75.0	−0.67	75.0	−0.24	85.0	0.98
80.0	−0.80	80.0	−0.33	90.0	0.84
85.0	−0.98	85.0	−0.45	95.0	0.58
		90.0	−0.64	99.0	0.31

H_2SO_4–HSO_3Cl					
Mol % HSO_3Cl	Log I	Mol % HSO_3Cl	Log I	Mol % HSO_3Cl	Log I
		p-Nitro-		*m*-Nitro-	
m-Nitrotoluene		chlorobenzene		chlorobenzene	
18.99	−0.35	4.1	0.57[a]	90.30	−0.18
32.80	−0.53	11.1	0.33[a]	100.0	−0.63
		24.8	0.06[a]		
Nitrobenzene		32.8	0.09	2,4-Dinitrotoluene	
18.99	−0.30	37.9	−0.03[a]	90.3	0.36
		54.6	−0.18[a]	95.0	0.26[a]
		69.8	−0.36[a]	97.5	0.11[a]
		81.0	−0.52[a]	100.0	−0.01[a]
		88.2	−0.63[a]	100.0	−0.08
		90.3	−0.90		

[a] Recalculation of Palm's data.[5]

nitrochlorobenzene, 2,4-dinitrotoluene, and 2,4-dinitrofluorobenzene. Determination of the ionization ratios for all the indicators was carried out by the spectrophotometric method. All of the nitro compounds have absorption maxima of their protonated forms in the region of 300–380 nm. The molar extinction coefficient was in all cases measured at the wavelength of maximum absorption even if this shifted slightly with changes in the composition of the acid media. Such solvent effects were in any case quite small. Values of the logarithm of the ionization ratio, $I = [BH^+]/[B]$, are give in Tables I and II.

Values of ϵ_{base} were determined in 95–98% H_2SO_4 as appropriate and values of ϵ_{ion} were determined in oleum solutions of appropriate strength or in dilute solutions of SbF_5 in HSO_3F. Some slight differences in the value of ϵ_{ion} obtained in the H_2SO_4–SO_3 system and that ob-

Table III. ϵ_{base}, ϵ_{ion}, λ_{max} (nm), and pK_{BH^+} Values for the Nitro Compound Indicators

Indicator	H_2O–H_2SO_4–SO_3				H_2SO_4–HSO_3F				Av
	ϵ_B	ϵ_{BH}	λ_{max}	pK_{BH^+}	ϵ_B	ϵ_{BH^+}	λ_{max}	pK_{BH^+}	pK_{BH^+}
2,4,6-Trinitroaniline	8,500	200	418	−10.10					−10.10
p-Nitrotoluene	2,100	19,200	376	−11.35					−11.35
m-Nitrotoluene	1,200	16,100	360	−11.99					−11.99
Nitrobenzene	900	15,150	348	−12.14					−12.14
p-Nitrofluorobenzene	600	16,500	360	−12.44					−12.44
p-Nitrochlorobenzene	400	21,800	386	−12.70	400	24,350	385	−12.70	−12.70
m-Nitrochlorobenzene	440	12,850	353	−13.20	440	14,380	348	−13.13	−13.16
2,4-Dinitrotoluene	1,700	13,900	339	−13.74	1,700	13,900	340	−13.76	−13.75
2,4-Dinitrofluorobenzene	920	12,100	336	(−14.03)	920	12,100	330	−14.52	−14.52

tained in the HSO_3F system were observed. Where possible, ionization ratios were calculated making use of ϵ_{ion} values for the particular super acid system under study. Values of ϵ_{base}, ϵ_{ion}, and the ionization constants (pK_{BH^+}) of the indicators are shown in Table III for the acid systems H_2O–H_2SO_4–SO_3 and H_2SO_4–HSO_3F. The values of ϵ_{ion} used for the systems H_2SO_4–$HB(HSO_4)_4$ and H_2SO_4–HSO_3Cl system were an average of those obtained for the H_2SO_4–HSO_3F and H_2O–H_2SO_4–SO_3 systems.

The pK_{BH^+} values for the indicators were determined by the overlap technique used originally by Hammett and Deyrup, and assuming the value of −10.10 given by Jorgenson and Hartter for the ionization constant of 2,4,6-trinitroaniline. This value was used rather than that of Johnson, *et al.*,[7] or Tickle, *et al.*,[8] as our measurements were carried out at room temperature (22 ± 1°). The pK_{BH^+} values increase with increasing temperature; thus the higher value of −10.03 as found by Johnson, *et al.*, at 25° is in good agreement. Tickle, *et al.*, found a value of −9.87 at 25° and −9.97 at 15° which are in rather marked disagreement with the results of Jorgenson, *et al.*, and Johnson, *et al.* We have made no attempts to check these differing values but have simply taken the value of −10.10 for the pK_{BH^+} of 2,4,6-trinitroaniline as the reference point of our work.

The weighting scheme of Johnson, *et al.*,[7] for the determination of the ionization constants is not used in the presentation of our results. Instead an average value of ΔpK_{BH^+} has been determined from the ionization ratio curves with the limitation that log I must lie between ±1. This is essentially a simplified weighting scheme which we have found leads to the same result as using Johnson's more time-consuming method. Johnson's method is more useful for the determination of the log I values of a number of different indicators in the same acid media. Our results are taken from curves of log I *vs.* acid composition where the averaging has been done by the drawing of the curve. Similarly H_0 values are calculated from unweighted averages and these average values plotted *vs.* acid composition. It was noted that the ionization ratio *vs.* acid composition curves are not straight lines. This is to be expected, as the H_0 function does not vary linearly with acid composition especially in the region of 100% H_2SO_4, HSO_3F, and HSO_3Cl. The ionization constants determined in the H_2SO_4–HSO_3F system were essentially identical with those found in the H_2O–H_2SO_4–SO_3 system. Where two pK_{BH^+} values for a single indicator could be independently determined the average values of the two was used. The pK_{BH^+} values so determined for the various indicators are listed in Table III.

The pK_{BH^+} value of 2,4-dinitrofluorobenzene in the H_2O–H_2SO_4–SO_3 system is noted to be much less than that found in the H_2SO_4–HSO_3F system. The behavior of this indicator in the very strong oleum solutions required to protonate it is rather unusual in that it appears to be parallel to the behavior of 2,4-dinitrotoluene over the range of 20–45 mol % SO_3 with a ΔpK_{BH^+} of 0.56. From 45 to 55 mol % SO_3 the ΔpK_{BH^+} decreases and from 55 to 65 mol % SO_3 it has the constant value of 0.28. This latter value gives a value of pK_{BH^+} for 2,4-dinitrofluorobenzene of −14.03. This indicator can be used for solutions containing SO_3 up to 75 mol % where the acidity of the H_2SO_4–SO_3 system appears to level off. The indicator 2,4-dinitrofluorobenzene is used in the H_2SO_4–SO system only over the range of 55–75 mol % SO_3. All H_0 values in this region are therefore somewhat uncertain. Ionization ratio measurements in the H_2SO_4–SO_3 system were not extended beyond 75 mol % SO_3 because the system becomes solid at room temperature and because suitable indicators appear to be unstable in the very strongly oxidizing medium.

It is important to show that the indicators form a valid set in that they give plots of log I *vs.* H_0 that are parallel and of unit slope. This may be conveniently tested by the method of Johnson, *et al.*,[7] who showed that in general one may write log $I_2 = a_{2,1}$ log $I_1 + a_{2,1}pK_1 - pK_2$ and $H_2 = a_{2,1}H_1$ where $a_{2,1}$ is a constant that measures the degree of parallellism of indicators 1 and 2 and should be unity for a pair of well-behaved indicators. H_2 and H_1 are acidity functions defined by indicators 2 and 1, respectively. The product $\Pi a_{i,i-1}$ indicates how the ith indicator behaves with respect to the acidity function H_1 defined by the first indicator. Individual $a_{i,i-1}$ values were obtained from plots of log I_i *vs.* log I_{i-1} and the results are given in Table IV.

Table IV

	$a_{i,i-1}$ = log (I_i/I_{i-1})	$\Pi a_{i,i-1}$
H_2O–H_2SO_4–SO_3 System		
p-Nitrotoluene	1.03	1.03
m-Nitrotoluene	1.00	1.04
Nitrobenzene	0.93	0.97
p-Nitrofluorobenzene	0.94	0.91
p-Nitrochlorobenzene	1.14	1.04
m-Nitrochlorobenzene	1.11	1.16
2,4-Dinitrotoluene	0.94	1.09
H_2SO_4–HSO_3F System		
m-Nitrochlorobenzene	1.00	1.04
2,4-Dinitrotoluene	1.00	1.04
2,4-Dinitrofluorobenzene	0.91	0.95

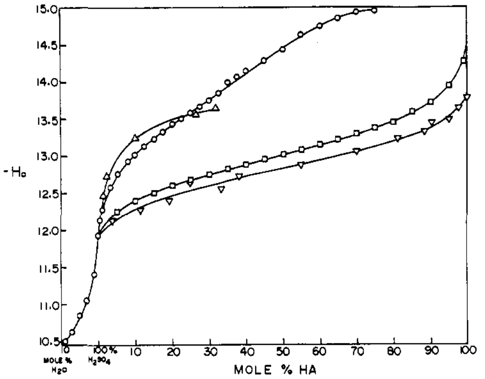

Figure 1. H_0 values for the systems: ○, H_2O–H_2SO_4–$H_2S_2O_7$; △, H_2SO_4–$HB(HSO_4)_4$; □, H_2SO_4–HSO_3F; ▽, H_2SO_4–HSO_3Cl.

The values of $a_{i,i\text{-}1}$ that we have obtained for our aromatic nitro compound indicators are quite comparable to those obtained by Johnson, *et al.*, for the primary aniline indicators, the scatter of the values from the expected value of unity being no greater than for the primary aniline indicators. The average $\Pi a_{i,i\text{-}1}$ value for the seven indicators used in the H_2O–H_2SO_4–SO_3 system is 1.03 and for the three indicators of the H_2SO_4–HSO_3F system it is 1.01.

The interpolated H_0 values for the super acid systems are shown in Tables V and VI and in Figure 1. Individual H_0 values were determined at integral acid compositions by taking the average of $[\mathrm{p}K_{\mathrm{BH}} - \log I]$ for each indicator used within the limitation that log I should not exceed ±1.

Table V. H_0 Values for the H_2O–H_2SO_4–SO_3 System

Wt % H_2SO_4	Mol % H_2O	$-H_0$	Wt % H_2SO_4	Mol % H_2O	$-H_0$
98.00	10.00	10.44	99.20	4.20	10.93
98.20	9.07	10.50	99.40	3.18	11.05
98.40	8.31	10.56	99.60	2.14	11.15
98.60	7.17	10.62	99.80	1.08	11.40
98.80	6.20	10.71	99.90	0.54	11.64
99.00	5.21	10.84	100.00	0.0	11.93
Mol % SO_3	**$-H_0$**	**Mol % SO_3**	**$-H_0$**	**Mol % SO_3**	**$-H_0$**
1.00	12.24	25.00	13.58	55.00	14.59
2.00	12.42	30.00	13.76	60.00	14.74
5.00	12.73	35.00	13.94	65.00	14.84
10.00	13.03	40.00	14.11	70.00	14.92
15.00	13.23	45.00	14.28	75.00	14.96
20.00	13.41	50.00	14.44		

Our H_0 measurements for the oleum system differ appreciably from those of Brand,[3,4] but the general trend is much the same. The reason for this difference lies mainly in the H_0 values for 100% H_2SO_4; Brand used a value of −10.89 whereas we find a value of −11.93. Application of a simple correction factor of −1.04 to Brand's data brings his H_0 values very close to ours. Solutions containing more than 25 mol % SO_3 have a freezing point above room temperature but if they are handled with care they remain as stable supercooled liquids at room temperature.

The rapid rise in the H_0 values for weak oleum solutions is due to the moderately large ionization[10] of $H_2S_2O_7$ (approximately 30% in a 0.1 *m* solution) according to the equation

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$$

which increases the $H_3SO_4^+$ concentration correspondingly. As the concentration of SO_3 increases, polysulfuric acids are formed according to[11,12]

$$H_2S_2O_7 + nSO_3 \rightleftharpoons H_2S_{n+2}O_{3n+7}$$

where $n = 1, 2, 3 \ldots.$ The acidity of the polysulfuric acid increases slightly with increasing chain length resulting in increasing H_0 values up to ~75 mol % SO_3. This composition corresponds to $H_2S_4O_{13}$ but in fact the solution contains a mixture of lower and higher polymers as well as some free SO_3. At higher SO_3 concentrations the formation of still higher polymers, *e.g.*, $H_2S_5O_{16}$, is probably incomplete with the result that the acidity appears to level off at an H_0 value of about −15.0.

Table VI. H_0 Values for the H_2SO_4–HSO_3F, H_2SO_4–HSO_3Cl, and H_2SO_4–$HB(HSO_4)_4$ Systems

Mol % $HB(HSO_4)_4$	$-H_0$	Mol % $HB(HSO_4)_4$	$-H_0$
1.00	12.35	10.00	13.23
2.00	12.60	15.00	13.39
4.00	12.87	20.00	13.49
6.00	13.03	25.00	13.56
8.00	13.15	30.00	13.62
Mol % HA	**$H_2S_2O_7$**	**HSO_3F**	**HSO_3Cl**
1.00	12.23	12.02	11.98
2.00	12.41	12.09	12.03
5.00	12.71	12.25	12.15
10.00	12.98	12.41	12.28
20.00	13.28	12.60	12.47
30.00	13.52	12.75	12.61
40.00	13.71	12.86	12.22
50.00	13.88	13.02	12.84
60.00	14.03	13.14	12.94
70.00	14.17	13.28	13.06
80.00	14.26	13.47	13.19
90.00	14.36	13.73	13.38
95.00	14.40	13.95	13.54
97.50	14.42	14.14	13.66
99.00	14.43	14.21	13.74
100.00	14.44		13.80

The initial increase in H_0 values for the super acid systems $HB(HSO_4)_4$–H_2SO_4, SO_3–H_2SO_4, HSO_3F–H_2SO_4, and HSO_3Cl–H_2SO_4 is greatest for $HB(HSO_4)_4$ and successively less for the other systems in the order $HB(HSO_4)_4 > SO_3\ (H_2S_2O_7) > HSO_3F > HSO_3Cl$. This reflects the decreasing ionization constants of these acids which have been found to be: $HB(HSO_4)_4$, 2×10^{-1}; $H_2S_2O_7$, 1.4×10^{-2}; HSO_3F, 2.3×10^{-3}; HSO_3Cl, 9×10^{-4}.

The very rapid rise in H_0 values upon the addition of $HB(HSO_4)_4$ to 100% H_2SO_4 is consistent with the fact that it is the strongest known acid of the H_2SO_4 system.[13] At concentrations of $HB(HSO_4)_4$ above 32 mol % a complex polymeric boron sulfate precipitates from solution, thus preventing the study of more concentrated solutions.

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After an initial rapid rise in the H_0 composition plots of the H_2SO_4–HSO_3X ($X = F, Cl$) systems, the plots become almost linear until about 80 mol % HSO_3X after which they again rise rather rapidly. The initial behavior is consistent with HSO_3F and HSO_3Cl being weak acids of the H_2SO_4 solvent system according to

$$HSO_3X + H_2SO_4 \rightleftarrows H_3SO_4^+ + SO_3X^-$$
$$X = F, Cl$$

Above 80 mol % HSO_3X, H_2SO_4 may be considered as a solute in the stronger acid solvent. In HSO_3Cl as solvent, H_2SO_4 acts as a very weak base and thus as the concentration of H_2SO_4 decreases the acidity begins to rise more rapidly. In HSO_3F as solvent, H_2SO_4 acts as a moderately weak base according to the above equation, hence increasing the concentration of SO_3F^-, the basic ion of the HSO_3F solvent system. As the concentration of H_2SO_4 decreases the SO_3F^- concentration also decreases and the extent of self-ionization of the solvent and the $H_2SO_3F^+$ concentration increases correspondingly.

$$2HSO_3F \rightleftarrows H_2SO_3F^+ + SO_3F^-$$

In the case of HSO_3F this increase is so rapid as to make the direct determination of the H_0 value for 100% HSO_3F very difficult. It is certainly greater than 14.5. Measurements on solutions of KSO_3F and SbF_5 in HSO_3F, which will be reported in a following paper,[9] enable the H_0 value of 100% HSO_3F to be determined with reasonable accuracy.

The original work of Palm[5] on the H_2SO_4–HSO_3Cl system was based upon an earlier, lower, H_0 value of 100% H_2SO_4 and on Brand's pK_{BH^+} values for *p*-nitrotoluene, *p*-nitrochlorobenzene, and 2,4-dinitrotoluene. Since we have revised these values our results do not agree with those of Palm. His corrected log *I* values are consistent with our measurements and we have used them to supplement our data for this system.

Experimental Section

Materials. 2,4,6-Trinitroaniline was recrystallized from glacial acetic acid. The solid nitro compound indicators *p*-nitrotoluene, *p*-nitrofluorobenzene, *p*-nitrochlorobenzene, *m*-nitrochlorobenzene, 2,4-dinitrotoluene, and 2,4-dinitrofluorobenzene were recrystallized from appropriate solvents and dried over standard desiccants. *m*-Nitrotoluene and nitrobenzene were dried over anhydrous magnesium sulfate and distilled at reduced pressure, the middle fraction being collected. They were further purified by fractional crystallization. All the indicators had melting points consistent with literature values.

Reagent grade sulfuric acid was adjusted to 100% H_2SO_4 by the addition of 30% oleum until the minimum conductivity or maximum freezing point was reached. The composition of H_2O–H_2SO_4 mixtures was checked by standard volumetric means. H_2SO_4–SO_3 mixtures were prepared by weight by the distillation of Sulfan (stabilized SO_3; Allied chemical) into 100% H_2SO_4.

H_2SO_4–HSO_3F and H_2SO_4–HSO_3Cl mixtures were prepared by weight. HSO_3F and HSO_3Cl were purified from commercial samples by simple fractional distillation at atmospheric and reduced pressure. Solutions of $HB(HSO_4)_4$ were prepared by the reaction of boric acid with a known concentration of $H_2S_2O_7$ in H_2SO_4 according to the equation

$$B(OH)_3 + 3H_2S_2O_7 \longrightarrow HB(HSO_4)_4 + 2H_2SO_4$$

Preparation of Solutions. Approximately 0.01 g of the indicator was weighed into a known weight of the stock acid mixture (10 g). From this an approximately 0.01-g aliquot was weighed into a 10-ml volumetric flask which was then diluted to the mark with the same stock acid mixture. After mixing, the resulting solution was syringed into a 1-cm cell and fitted with a Teflon cap. At the same time a reference sample was prepared from the stock acid mixture. Operations were generally carried out in a S. Blickman, Inc. vacuum drybox equipped with an analytical balance.

Spectrophotometric Measurements. All measurements were carried out with matched quartz glass Suprasil 1-cm cells fitted with a standard taper 7.5 top and Teflon stoppers (Hellma Ltd.). Spectra were recorded at room temperature (22°) with a Cary Model 14 recording spectrophotometer. The reference material way always of the same stock acid mixture as that used in preparation of the indicator solutions.

The ionization ratios, *I*, were obtained from the expression $(\epsilon_{BH^+} - \epsilon)/(\epsilon - \epsilon_B)$, where ϵ_B and ϵ_{BH^+} are the extinction coefficients of the unprotonated and fully protonated forms of the base. ϵ, the extinction coefficient of the indicator in any given solution, was measured directly from the absorption spectra. In some cases log *I* values were determined at integral acid compositions using ϵ values obtained from an ϵ *vs.* acid composition curve.

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