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Operational Scale of Hydronium Ion Activities for Strongly Acidic Media

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Abstract: The new acidity function, H_{GF}, established previously for aqueous solutions of H_2SO_4 and $HClO_4$ by a combined polarographic-glass electrode approach with the ferrocene-ferricenium couple as reference, has been extended to solutions of H_3PO_4, H_3PO_3, and methanesulfonic and *p*-toluenesulfonic acids. The variation of the activity coefficients of ferrocene and ferricenium ion with acid concentration has been determined for all six acids by distribution and solubility methods. These data, combined with H_{GF} values, have made it possible to calculate, for these media proton activities, log a_{H^+}, relative to the standard ion (TEA$^+$). The resulting acidity scale is considered to be a better operational measure of acidity in concentrated acids than spectrophotometrically determined acidity functions. Its potential utility in mechanistic studies of acid-catalyzed reactions is discussed.

As an operational measure of the acidity of nondilute acid solutions, the acidity function approach has serious shortcomings, particularly for the interpretation of rate-acidity dependence in concentrated acids. These difficulties arise mainly from the presence of the indicator activity coefficient ratios which are inherent in the definition of any generalized acidity function H_x, *i.e.*

$$H_x = -\log(a_{H^+}f_x/f_{XH^+})$$
$$= pK_{XH^+} - \log(C_{XH^+}/C_X)$$

Because of the specific interactions between the indicator species X and XH^+ and the medium, these ratios frequently show highly individualistic behavior. Although several classes of indicator base generate reasonably well-behaved acidity functions, there are still problems associated with anchoring the acidity scales to ideal dilute aqueous solution as standard state and also with the standard overlap technique of determining acidity functions. Because overlapping pairs of different indicator bases must be used, and parallelism of ionization ratio behavior is not always perfect, cumulative errors of uncertain magnitude are introduced.

To avoid these problems, attempts have been made to estimate or determine the hydronium ion activities of concentrated acid solutions directly. Since single ion activities are themselves inaccessible, such values of hydronium ion activity are always related to some standard ion (Z^+) in the form of a ratio, *i.e.*

$$a^*_{H^+} = a_{H^+}/f_{Z^+}$$

We have recently reported estimates of the hydronium ion activity in aqueous sulfuric acids up to 70% acid.[3] These were based on five independent acidity scales, combined with independently measured activity coefficient data on appropriate model indicator species, using the relation

$$\log a^*_{H^+} = -H_x - \log f_X + \log f^*_{XH^+}$$

Since the model cation activity coefficients are necessarily referred to some standard ion, using the Boyd approximation,[4] the resulting hydronium ion activities are thus referred to the same standard ion, in this case tetraethylammonium (TEA^+). Hence, $\log a^*_{H^+} = \log a_{H^+}/f_{TEA^+}$. The internal agreement between the five independent estimates of $\log a^*_{H^+}$ was remarkably good in view of the approximations involved.

Recently, Janata and Jansen[5] have employed a more direct electrochemical method of measuring hydronium ion activities using combined polarographic-glass electrode measurements in a cell involving no liquid junction and the ferrocene-ferricenium ion (Fec-Fec^+) couple as a reference electrode. The function H_{GF} is there based on the measured difference E between the ferrocene half-wave potential $E_{1/2}$ and the glass electrode potential E_g. These potentials are

$$E_{1/2} = E°_{1/2} - (2.303RT/F)[\log(f_{Fec}/f_{Fec^+}) + {}^1/_2 \log(D_{Fec^+}/D_{Fec})]$$

and

$$E_g = E°_g + (2.303RT/F)\log a_{H^+}$$

where $E°$ represent potentials in standard solutions and f and D are the activity and diffusion coefficients of ferrocene and ferricenium ion. The measured difference is

$$E = (E_{1/2} - E_g) = (E°_{1/2} - E°_g) - (2.303RT/F) \times [\log a_{H^+} + \log(f_{Fec}/f_{Fec^+}) + {}^1/_2 \log(D_{Fec^+}/D_{Fec})]$$

and the acidity function is defined as

$$H_{GF} = (F/2.303RT)[(E°_{1/2} - E_{1/2}) - (E°_g - E_g)] - {}^1/_2 \log(D_{Fec^+}/D_{Fec})$$

Therefore the acidity scale they determined was effectively defined by

$$-H_{GF} = \log a_{H^+} + \log(f_{Fec}/f_{Fec^+})$$

The ferrocene-ferricenium couple at DME satisfies the usual requirements for a reference electrode; its electrode potential was shown to be reversible, and any side reactions involving the redox couple are too slow to affect the measurements taken at the dropping mercury electrode. The assumption that the ratio of diffusion coefficients remains constant for various media is frequently made in polarography, and we believe that it is also true in our case, due to the very low solvation of both ferrocene and ferricenium ion.

The advantage of this approach is that only one pair of activity coefficients is involved at all acidities, unlike in the standard acidity function approach.

These two scales of hydronium activity (H_{GF} and $\log a^*_{H^+}$) can be compared directly by adjusting the H_{GF} function to the same reference basis (TEA^+) as the estimated $\log a^*_{H^+}$ scale. This involves measurement of the activity coefficient behavior of ferrocene and ferricenium ion in the acid solutions of interest. Thus

$$H_{GF} - \log f^*_{Fec^+} + \log f_{Fec} = \log a^*_{H^+}$$

where $f^*_{Fec^+}$ is also referred to the standard ion TEA^+. Such a comparison has been made and reported in a preliminary communication.[6] Since the agreement obtained was highly satisfactory, it seemed very desirable to extend the polarographic-glass electrode measurements of hydronium ion activity to other acid solutions and to correct these to the commonly adopted reference ion TEA^+ by determining appropriate activity coefficients of ferrocene and ferricenium salts.

The particular choice of TEA^+ as reference ion rather than Fec^+ was made on two bases. Firstly, for the reasons discussed by Boyd, the tetraethylammonium ion should be relatively free of medium-dependent specific solute-solvent interactions;[7] and, secondly, a large body of activity coefficient data is already available which has been referred to this standard ion.

Experimental Section

Acidity Function Measurements. The half-wave potential of ferrocene was determined as described previously.[5] Approximately 90% methanesulfonic acid was prepared, and the concentration of this solution was determined by titration with 0.1 *N* NaOH. Approximately 15 ml of this solution was then weighed differentially into the polarographic vessel, and a few crystals of ferrocene were added. More dilute solutions were obtained by pipetting in accurately appropriate amounts of saturated aqueous solution of ferrocene. The H_{GF} acidity function for *p*-toluenesulfonic acid was obtained in a similar manner by starting off with a nearly saturated solution of the acid. For phosphoric and phosphorous acids, solutions were prepared by a differential weighing of 15 ml of the concentrated acid of known concentration followed by successive additions of saturated aqueous solution of ferrocene and some crystals of ferrocene. Freshly prepared solutions were used for the measurements.

Activity Coefficient Measurements. Acid Solutions. All solutions were prepared by diluting the appropriate concentrated acid of AnalaR Grade with doubly distilled water. Methanesulfonic acid (Eastman) was distilled under vacuum, and the fraction boiling at 164–165° (1.5 mm) was collected. *p*-Toluenesulfonic acid monohydrate (BDH) was crystallized from water, mp 104–105°. Concentrations of aqueous solutions of sulfuric, perchloric, and phosphoric acids were determined from their densities measured with a DMA 02C digital precision density meter at 25.0°. For the remaining acids, the concentration of stock concentrated solution was determined by standard titration against sodium hydroxide, and the individual solutions were prepared by weighing out an appropriate amount of acid and adding a known volume of water.

Compounds Used for Activity Coefficient Measurements. Ferrocene (Eastman) was crystallized from heptane: mp 176–176.5° (lit.[8] 173–174°); λ_{max} (H_2O) 199 nm (ϵ 43,300); λ_{sh} 250 nm (ϵ 8000). Tetraethylammonium pentacyanopropenide was prepared by the method of Middleton, *et al.*,[9] mp 220–221° (from water-ethanol, 10:1) (lit. 220–221°). Ferricenium pentacyanopropenide was prepared according to Harbison[10] by reaction of 1,1,2,3,3-pen-

Table I

% (w/w) acid	$d^{25°}$	% (w/w) acid	$d^{25°}$
H_3PO_3		CH_3SO_3H	
10.0	1.0454	25.0	1.1100
15.0	1.0697	30.0	1.1385
20.0	1.0953	40.0	1.1900
25.0	1.1202	45.0	1.2162
30.0	1.1502	50.0	1.2437
40.0	1.2112	60.0	1.2922
		$C_7H_7SO_3H$	
50.0	1.2749	10.35	1.0300
60.0	1.3427	20.0	1.0556
70.0	1.4170	30.0	1.0960
CH_3SO_3H			
10.0	1.0416	40.0	1.1314
15.0	1.0629	53.5	1.1801
20.0	1.0867		

tacyanopropene with ferricenium tetrachloroferrate: yield 80%; λ_{max} (H_2O) 250 nm (ϵ 13,300), 397 (22,800) (literature values for Fec^+ ion[11] λ_{max} 250 nm, ϵ 12,000; for PCP^- ion[4] λ_{max} 410 nm, ϵ 23,000).

Anal. Calcd for $C_{18}H_{10}N_5Fe$: C, 61.39; H, 2.86; N, 19.89. Found: C, 60.79; H, 2.90; N, 19.99.

Distribution Method. One milliliter of a *ca.* 2.5 × 10^{-2} *M* solution of ferrocene in cyclohexane (ACS Spectranalyzed Grade) was shaken mechanically with 3-4 ml of water or the aqueous acid solution for 1 min in a thermostatically controlled (25 ± 0.1°) glove box. Separate experiments showed this time to be sufficient to obtain equilibration. The aqueous layer was transferred to the uv cell, and the absorbance of ferrocene was measured at 199 nm, using a Cary 14 recording spectrophotometer. In most cases, the decrease of the absorbance with time was recorded, and the initial value of the absorbance was obtained by extrapolation to zero shaking time. The values of the activity coefficient were then calculated from the ratio of the absorbance in pure water to that in a given acid solution.

For the solutions of *p*-toluenesulfonic acid, after equilibration, 5 ml of the aqueous layer was extracted with cyclohexane (3 × 4 ml), and the combined cyclohexane extracts were dried ($MgSO_4$) and evaporated under reduced pressure to a volume of 1 drop. The residue was then transferred quantitatively (the flask was washed successively with 3 drops of cyclohexane) on one part of a tlc plate, covered with aluminum oxide (CAMAG, without $CaSO_4$), and divided vertically into two parts. The authentic sample of ferrocene solution was placed at the second part of the plate, and the plate was developed with cyclohexane (under these conditions R_f values for ferrocene and *p*-toluenesulfonic acid are 0.68-0.70 and 0.00, respectively). After developing, the adsorbent section at the distance corresponding to the colored spot of the authentic ferrocene sample was removed and extracted with a known volume of cyclohexane, and the concentration of ferrocene in this solution was measured in the usual way.

Solubility Method. TEA^+PCP^- (10^{-5}-8 × 10^{-5} mol) or 3 × 10^{-5}-1.5 × 10^{-4} mol of Fec^+PCP^- (finely ground before measurement) was shaken with 1 ml of water or the appropriate aqueous acid solution at 25 ± 0.1° for 4-7 hr. The saturated solution obtained was then filtered through a fritted disk (medium) into a tared weighing bottle using a slight positive pressure, the bottle with its contents was weighed, and the solution was diluted to the required concentration with water or the appropriate aqueous acid. The concentration of the salt was then determined from the absorbance of the solution at 397 nm.

Density Measurements. In order to convert various values of activity coefficients and acidity values from the commonly used per cent (w/w) scale to the molarity scale, the densities of the aqueous acids are needed. These are readily available for H_2SO_4, $HClO_4$, and H_3PO_4, but it was necessary to measure appropriate values for the other three acids. These were obtained using an Anton Paar Model DMA02C digital precision density meter and are listed in Table I.

Results

Values of the glass-ferrocene function $-H_{GF}$ for aqueous solutions of H_3PO_4, H_3PO_3, CH_3SO_3H, and $C_7H_7SO_3H$ have been obtained as before[5] and are listed in Table II. Values for H_2SO_4 and $HClO_4$ have already been reported.[5]

Table II. Values of the Acidity Function $-H_{GF}$ at 25.0°

	$-H_{GF}$			
% acid	H_3PO_4[a]	H_3PO_3	CH_3SO_3H	$C_7H_7SO_3H$
1.0			−0.75	−1.45
2.5	−1.29	−1.73	−0.58	−1.13
5.0	−0.94	−0.76	−0.32	−0.78
7.5	−0.55	−0.51	−0.05	−0.52
10.0	−0.20	−0.32	0.06	−0.30
15.0	0.43	−0.13	0.38	−0.02
20.0	0.99	−0.01	0.67	0.12
25.0	1.51	0.12	0.94	0.21
30.0	2.05	0.29	1.19	0.31
35.0	2.62	0.51	1.40	0.42
40.0	3.26	0.74	1.65	0.59
45.0	4.04	1.00	1.95	0.80
50.0	4.97	1.25	2.26	1.05
55.0	6.08	1.51	2.65	1.32
60.0	7.42	1.80	3.10	1.75
65.0		2.14	3.55	[b]
70.0		2.57	4.15	
75.0		3.10	4.83	
80.0		3.74	5.67	
85.0		4.43	6.55	
90.0			7.70[c]	

[a] Given as % P_2O_5. [b] Last measured value was for 62.5%, 2.30. [c] Estimated; last measured value was for 87.6%, 7.27.

Activity coefficient behavior of ferrocene was determined in all six acids by the distribution method. Since the distribution coefficient for partitioning between the organic phase (cyclohexane) and water or aqueous acid solution is very small (*ca.* 10^{-3}), the concentration of ferrocene in the cyclohexane layer was taken as constant, and activity coefficients were calculated directly from the ratio of the absorbance in pure water to that in the acid solution.

The instability of ferrocene in strong acid solutions is well known,[11,12] the ferricenium cation (Fec^+) being the primary product of decomposition. Although in distribution experiments equilibration is effectively completed after 1 min of shaking, and the uv spectrum of the aqueous phase could be recorded in less than 3 min, we found that for all concentrations of H_2SO_4, $HClO_4$, H_3PO_4, H_3PO_3 and above 30% of CH_3SO_3H solutions, various amounts of ferrocene had been oxidized to ferricenium ion over the time of measurement. When the decomposition was relatively slow, the concentration of ferrocene could be determined by following the decrease of its absorption at 199 nm with time and extrapolating spectral data back to zero equilibration time. However, for all acids above a certain concentration, the oxidation appeared too fast to make extrapolation possible. The experimental values of f_{Fec} are, therefore, limited mainly to the moderate concentrations of acids, and at higher acidities, extrapolation of plots of log f_{Fec} *vs.* acidity was necessary.[13]

In solutions of *p*-toluenesulfonic acid, an additional difficulty was encountered. Since this medium absorbs strongly in the near uv region, the concentration of ferrocene could not be determined at 199 nm, *i.e.*, from its high-intensity absorption band (log ϵ 4.63). The low-intensity band in the visible region (log ϵ 1.96 at 440 nm) was of no use because of the low concentrations of the solute. In this case, the aqueous acid solution after equilibration was reextracted immediately with pure cyclohexane to give cyclohexane solution containing the equilibrated amount of ferrocene and some *p*-toluenesulfonic acid. This solution was dried and concentrated to small volume, and the residue was separated by means of quantitative tlc; the ferrocene-containing fraction was extracted with cyclohexane and examined spectroscopically in the usual way. Preliminary experiments

Table III. Activity Coefficients of Ferrocene at 25.0°

% acid	Log f_{Fec}					
	H_2SO_4[a]	$HClO_4$[a]	H_3PO_4[a]	H_3PO_3[a]	CH_3SO_3H	$C_7H_7SO_3H$[c]
5.0	0.08	−0.12	−0.06	−0.02	−0.02 [b]	−0.02
10.0	0.14	−0.23	−0.11	−0.06	−0.04	−0.05
15.0	0.19	−0.31	−0.14	−0.13	−0.08	−0.10
20.0	0.22	−0.38	−0.16	−0.20	−0.13	−0.19
25.0	0.21	−0.43	−0.17	−0.28	−0.19	−0.32
30.0	0.17	−0.47		−0.36	−0.27	−0.49
35.0	0.09[d]	−0.51			−0.37	−0.73
40.0		−0.54[e]			−0.47 [a]	−1.00
45.0					−0.59	
50.0					−0.72	
55.0					−0.85	
60.0					−0.98	

[a] Obtained by extrapolation to zero equilibration time. [b] Obtained directly without extrapolation. [c] Obtained by quantitative tlc separation method. [d] Last measured value was for 34.3%, 0.10. [e] Last measured value was for 39.4%, −0.52.

showed that the recovery of ferrocene is practically quantitative.

The activity coefficients of ferrocene obtained in all six acids at different concentrations are listed in Table III.

Medium variation of the activity coefficients in sulfuric and perchloric acid solutions is similar to the behavior observed for numerous neutral compounds in these media.[14] In H_2SO_4, ferrocene is initially weakly salted out and then salted in at acid concentrations above 40%; in $HClO_4$, the salting-in effect occurs immediately. For other media, data for comparison are not available; in all cases, the immediate salting-in effect was observed. This effect is strongest in solutions of *p*-toluenesulfonic acid, which seems reasonable in terms of the aromatic character of both solvent and solute molecules.

Activity coefficients for ferricenium pentacyanopropenide (Fec^+PCP^-) were obtained by the solubility method described previously by Boyd.[4] The solubilities of the salt gave the log $f^*_{Fec^+}$ values (relative to tetraethylammonium ion as standard reference) according to the equation:

$$f^*_{Fec^+} \equiv f_{Fec^+}/f_{TEA^+} = \frac{f_{Fec^+}f_{PCP^-}}{f_{TEA^+}f_{PCP^-}} = [f_{\pm(Fec^+PCP^-)}/f_{\pm(TEA^+PCP^-)}]^2$$

Preliminary values of $f_{\pm(TEA^+PCP^-)}$ in H_2SO_4[4] and $HClO_4$[3] solutions have been reported previously; for the remaining four acid systems, they were determined in the present work by the solubility method. For both salts, solubility measurements were based on the absorbance of the PCP^- ion (λ_{max} 397 nm). In the case of Fec^+PCP^-, where the solubility could be determined from cation (λ_{max} 250 nm) and/or anion absorption bands, we found that the $[Fec^+]/[PCP^-]$ ratio varied slightly with acid concentration and was usually slightly higher than unity. This could indicate some extent of protonation of PCP^- in acid AH, followed by the transfer of some Fec^+ ions in the form of Fec^+A^- salt to the equilibrated solution. Since we were interested in solubilities of Fec^+PCP^- species only, it was assumed that the absorbance of PCP^- ion is the most reliable measure of the solubility of this salt in a given acid solution. The activity coefficients of both pentacyanopropenide salts in different acids solutions are collected in Table IV.

The activity coefficient data, combined with the values of the H_{GF} acidity function determined in the present and previous work,[5] made it possible to calculate the proton activities according to the equation:

$$\log a^*_{H^+} = -H_{GF} + \log f^*_{Fec^+} - \log f_{Fec}$$

The values of log $a^*_{H^+}$ taken at 0.5 *M* intervals in aqueous solutions of six acids are listed in Table V.

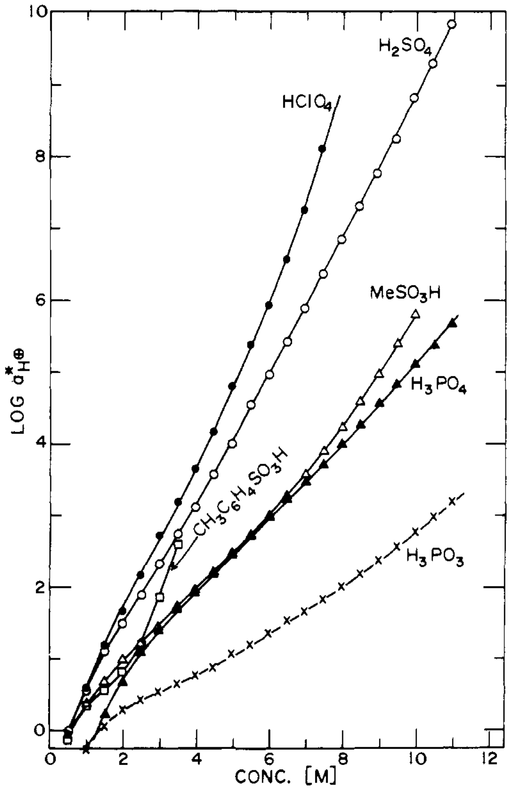

Figure 1. The variation of hydronium activity (log $a^*_{H^+}$) with acid concentration.

Discussion

The variation of hydronium activity (log $a^*_{H^+}$) with acid concentration (molarity)[15] is shown graphically in Figure 1, from which it can be seen that perchloric acid is the strongest of the six acids, as expected. Sulfuric acid is weaker in terms of hydronium ion activity by a factor of between 10 and 100 over most of the concentration range studied but is still much stronger than the other acids. The two sulfonic acids are next in order of strength, as might be expected, since this type of acid is normally almost completely ionized in dilute aqueous solution. However, the hydronium ion activity variation of aqueous *p*-toluenesulfonic acid is somewhat anomalous compared with the other acids. This is presumably because as the water in the solution is replaced by acid, the medium becomes more and more hydrocarbon like, and the hydronium ion is increasingly salted out. Although the two phosphorus-containing acids are the weakest, the behavior of phosphoric acid is interesting. In dilute solution, where both H_3PO_4 and H_3PO_3 are incompletely ionized, the first dissociation constants indicate that H_3PO_3

Table IV. Activity Coefficients of TEA^+PCP^- and Fec^+PCP^- at 25.0°

% acid	H_3PO_4	H_3PO_3	CH_3SO_3H	$C_7H_7SO_3H$	H_2SO_4	$HClO_4$
			(a) Log f_{PCP^-}[a]			
5.0	−0.14	−0.29	−0.36	−0.60		
10.0	−0.22	−0.36	−0.51	−1.10		
15.0	−0.28	−0.45	−0.60	−1.48		
20.0	−0.33	−0.56	−0.69	−1.80		
25.0	−0.40	−0.68	−0.80	−2.10		
30.0	−0.48	−0.84	−0.94	−2.36		
35.0	−0.58	−0.99	−1.09	−2.61		
40.0	−0.72	−1.15	−1.24	−2.83		
45.0	−0.87	−1.33	−1.40	−3.02		
50.0	−1.04	−1.52	−1.56	−3.19		
55.0	−1.25	−1.72	−1.72			
60.0	−1.50	−1.94	−1.90			
65.0	−1.79	−2.17	−2.12			
70.0	−2.16	−2.40	−2.35			
			(b) Log $f^*_{Fec^+}$[b]			
5.0	0.14	0.15	0.21	0.19	0.32	−0.02
10.0	0.24	0.23	0.28	0.24	0.42	−0.03
15.0	0.32	0.27	0.30	0.21	0.42	−0.02
20.0	0.36	0.26	0.31	0.14	0.42	0.00
25.0	0.38	0.23	0.30	0.09	0.42	0.04
30.0	0.37	0.17	0.29	0.05	0.44	0.09
35.0	0.36	0.11	0.29	0.03	0.48	0.17
40.0	0.35	0.05	0.28	0.02	0.50	0.26
45.0	0.33	0.01	0.27	0.01	0.54	0.39
50.0	0.32	−0.02	0.26	0.01	0.54	0.61
55.0	0.30	−0.04	0.25	0.01	0.52	0.90
60.0	0.28	−0.05	0.24		0.56	1.32
65.0	0.27	−0.04			0.55	
70.0	0.25	−0.03			0.60	

[a] $f_{PCP^-} = f_{TEA^+}f_{PCP^-} = [f_{\pm(TEA^+PCP^-)}]^2$. [b] $f^*_{Fec^+} = [f_{\pm(Fec^+PCP^-)}/f_{\pm(TEA^+PCP^-)}]^2$.

Table V. Hydronium Ion Activities at 25.0°

	Log $a^*_{H^+}$					
Acid concn, *M*	H_2SO_4	$HClO_4$	H_3PO_4	H_3PO_3	CH_3SO_3H	$C_7H_7SO_3H$
0.5	−0.06	−0.03		−0.72	−0.07	−0.18
1.0	0.54	0.58	−0.35	−0.22	0.37	0.34
1.5	1.10	1.18	0.21	0.06	0.68	0.55
2.0	1.49	1.67	0.67	0.28	0.98	0.80
2.5	1.89	2.17	1.08	0.41	1.21	1.25
3.0	2.32	2.72	1.37	0.54	1.44	1.87
3.5	2.73	3.18	1.67	0.64	1.72	2.59
4.0	3.11	3.65	1.90	0.75	1.93	3.72
4.5	3.57	4.16	2.17	0.87	2.18	4.16
5.0	4.00	4.80	2.42	1.06	2.43	
5.5	4.55	5.38	2.69	1.19	2.70	
6.0	4.96	5.94	2.97	1.35	2.97	
6.5	5.42	6.56	3.22	1.51	3.26	
7.0	5.89	7.26	3.47	1.65	3.56	
7.5	6.37	8.11	3.72	1.82	3.89	
8.0	6.85		3.99	2.00	4.24	
8.5	7.31		4.27	2.18	4.59	
9.0	7.77		4.57	2.37	4.97	
9.5	8.25		4.82	2.55	5.40	
10.0	8.82		5.11	2.75	5.78	
10.5	9.29		5.36	2.97		
11.0	9.87		5.66	3.18		

is the stronger acid. This is in agreement with tabulated p*K* values of 2.12 for H_3PO_4 and 2.00 for H_3PO_3.[16] However, in more concentrated solutions, H_3PO_4 becomes increasingly stronger. (Note that the log $a^*_{H^+}$ curves for H_3PO_4 and H_3PO_3 cross at about 1 *M* acid.) The reason for this is not clear in terms of the structures of these two acids or their anions.

In the past, considerable attention has been paid to the water activity as an important factor in determining the acidity of strongly acid solutions.[17] However, the curves of log $a^*_{H^+}$ *vs.* log a_{H_2O} for H_2SO_4 and $HClO_4$ as shown in Figure 2 clearly do not give any simple relationship between hydronium ion activity and water activity. Certainly, the hydronium ion activities of these two acids are not a unique function of a_{H_2O}, as sometimes is found to be the case for acidity functions. It is difficult to conclude that the water activity itself is a prime factor in controlling the acidity when (for these two acids at least) log $a^*_{H^+}$ changes by several powers of ten before a_{H_2O} is significantly lowered from its value in dilute solution. It is more likely that changes in solvent structure which occur when acid is added to pure water are more responsible for such drastic changes in hydronium ion activity.

It has been pointed out[5] that potentiometrically deter-

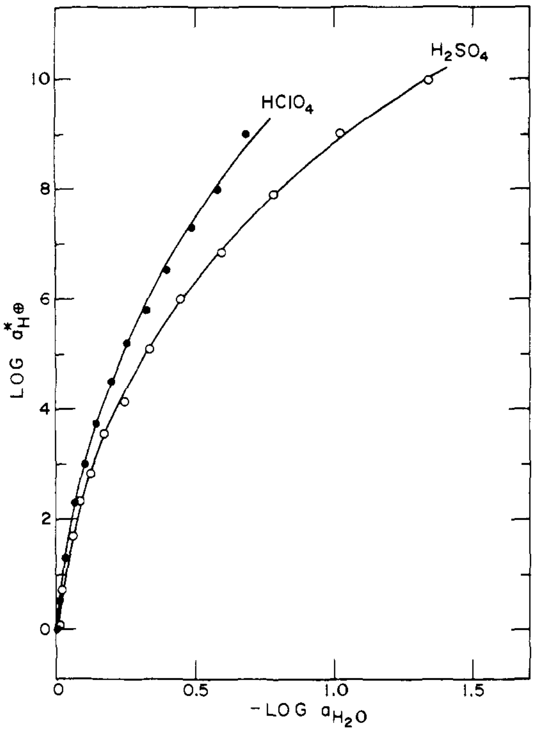

Figure 2. Plots of log $a^*_{H^+}$ *vs.* logarithmic water activity for sulfuric and perchloric acid solutions.

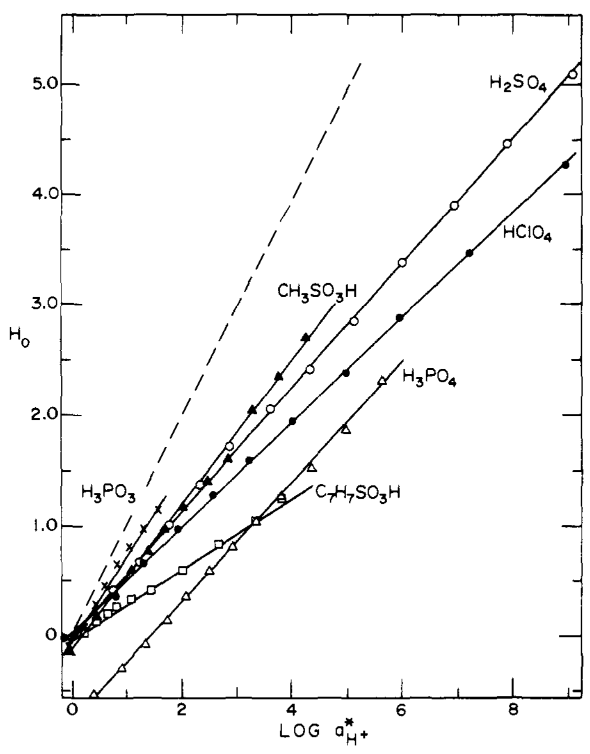

Figure 3. The relationship between H_0 and log $a^*_{H^+}$ in aqueous acids.

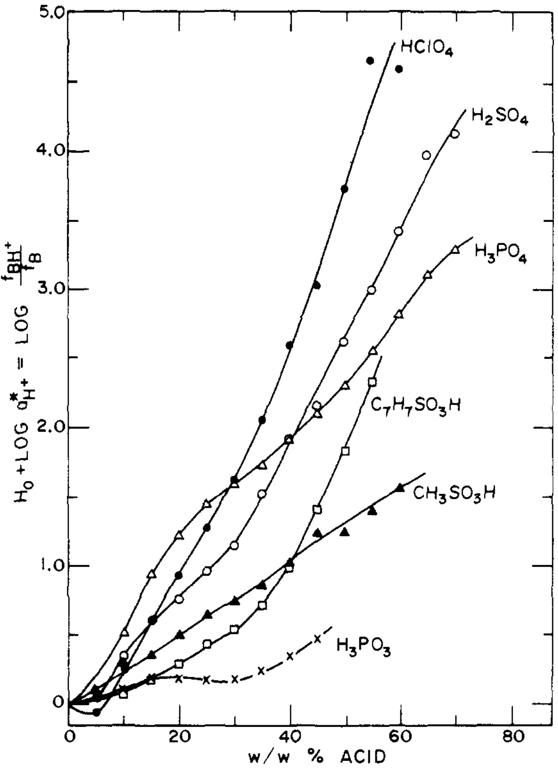

Figure 4. Dependence on calculated values of log $f^*_{BH^+}/f_B$ upon acid concentration.

mined acidity scales of the present type are fundamentally different from spectrophotometrically determined acidity functions of the H_0 type and hence can be used to assess these functions independently. An excellent 1:1 relationship has been shown to exist[5] between H_{GF} and the H_C function (for H_2SO_4 and $HClO_4$) which is based on protonation of carbon bases. This suggested that the carbon bases and their conjugate carbonium ions are essentially unaffected by specific solvation effects, and that the ratio of their activity coefficients remains virtually constant with medium. Unfortunately, the only acidity function which has been determined in all six acids studied here is the H_0 function. Figure 3 shows the relationship between H_0 and log $a^*_{H^+}$, from which it can be seen that the two scales are remarkably linear with respect to each other. However, it is difficult to attribute any fundamental significance to such linear relationships, for the following reasons. Firstly, as dilute solution is approached, both acidity scales must approach the pH scale (and, in fact, they have been demonstrated to do so) and hence must become identical in the limit for any acid. Thus, the limiting value of all the slopes in Figure 3 must be unity. The slopes in Figure 3 in the more concentrated region are clearly far from unity (indicated by the dashed line).

Secondly, the quantity H_0 + log $a^*_{H^+}$, according to the definition of the acidity function, is equal to the (logarithmic) activity coefficient ratio which is determined by the behavior of the primary aniline indicators used to establish H_0, *i.e.*

$$H_0 = -\log (a_{H^+} f_B / f_{BH^+})$$

$$H_0 + \log a^*_{H^+} = -\log (f_B f_{TEA^+} / f_{BH^+}) = \log (f^*_{BH^+} / f_B)$$

where $f^*_{BH^+}$ is referred to TEA$^+$ as standard ion. According to the Hammett activity coefficient postulate,[17,18] each pair of indicator bases whose overlapping ionization behavior is used to establish H_0 should have the same value of log f_{BH^+}/f_B or log $f^*_{BH^+}/f_B$. Hence, values of log $f^*_{BH^+}/f_B$, calculated as above, should be a smooth and probably gradually monotonic[19] function of acid concentration. Values of log $f^*_{BH^+}/f_B$ *vs.* % acid are shown in Figure 4 for all six acids. It appears that only for $HClO_4$ and CH_3SO_3H solutions is this requirement reasonably well satisfied. For the other four acids, log $f^*_{BH^+}/f_B$ is either a somewhat irregular function of acid concentration or else is monotonic but sharply changing with concentration. This strongly suggests that the Hammett postulate is not being obeyed very well in general, and that the parallelism of indicator ionization curves is considerably less perfect than would be hoped for.

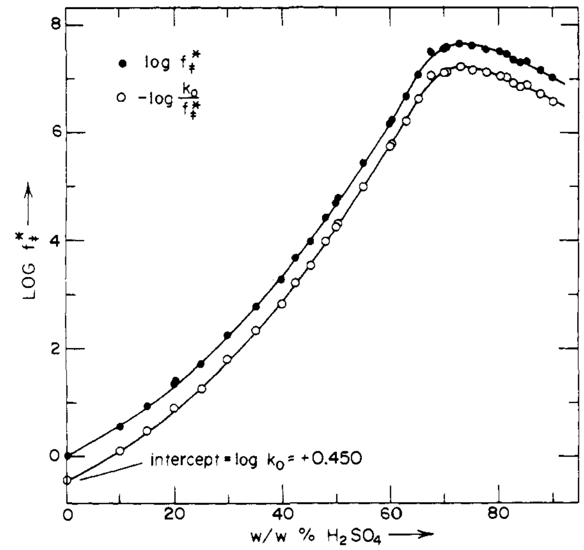

Figure 5. Plot of log $k_0/f^*_{\neq}$ and log $f^*_{\neq}$ *vs.* concentration of sulfuric acid for the hydrolysis of methyl *o*-toluate.

In other words, H_0 scales in these acids are probably not very well-behaved functions, and uncertainties due to cumulative errors in determining H_0 type functions could be quite serious, especially at very high acid concentrations.

For this and other reasons, it seems perferable to use potentiometrically determined acidity scales of the type described in this paper as operational measures of acidity in concentrated acid solutions. This is particularly true in our view for interpretations of the kinetic-acidity dependence of acid-catalyzed reactions.

Of the various kinetic treatments available for reactions in nondilute acids, each has its attendant uncertainties or ambiguities. These arise either because of necessary assumptions about cancellation of certain activity coefficient ratios or assumptions concerning the role of the water activity.[20] A simpler treatment can be proposed which is based on transition-state theory and uses hydronium ion activities directly. This approach does not involve any assumptions concerning the acidity function behavior of a particular substrate, nor does it involve the water activity of the medium since it is not a hydration parameter treatment.

If we consider any acid-catalyzed reaction of the common type

$$S + H^+ \overset{\text{fast}}{\rightleftharpoons} SH^+$$

$$SH^+ \xrightarrow{\text{slow}} S^{\ddagger} \longrightarrow \text{products}$$

the rate equation based on transition-state theory is simply

$$V = \frac{k_0}{K_{SH^+}}[S]\frac{f_S}{f_{S^{\ddagger}}}$$

where K_{SH^+} is the dissociation constant of protonated substrate. From this, the logarithm of the pseudo-first-order rate constant is given by:

$$\log k_{\psi} = \log k_0 - \log K_{SH^+} + \log f_S - \log f_{S^{\ddagger}} + \log a_{H^+}$$

Of the various terms in this expression, all can be determined in a given case except log k_0 and log $f_{S^{\ddagger}}$. Values of K_{SH^+} can usually be estimated reasonably accurately if the substrate is not too rapidly hydrolyzed. Similarly, log f_S can be measured directly for the substrate itself by distribution measurements. Values of log a_{H^+} (relative to TEA$^+$) are now available, and log k_{ψ} can easily be measured as a function of acid concentration. Therefore:

$$\log \frac{k_0}{f_{S^{\ddagger}}} = \log k_{\psi} + \log K_{SH^+} - \log f_S - \log a_{H^+} = f(\text{acid concentration})$$

Since all the individual terms on the right of this expression can be obtained in a given case, it is possible to plot log $k_0/f_{S^{\ddagger}}$ as a function of acid concentration, as shown for a specific example in Figure 5.[21] Since log $f_{S^{\ddagger}}$ must approach zero in ideal dilute solution, the intercept of this curve is given by log k_0. Hence, log $f_{S^{\ddagger}}$ itself can be determined (as shown by the parallel curve). Therefore, it is possible for the first time to estimate the medium variation of transition-state activity coefficients (relative to some standard ion) for a variety of acid-catalyzed reactions. In the particular case shown, the hydrolysis of methyl *o*-toluate, the variation of log $f_{S^{\ddagger}}$ is characterized initially by a strong salting-out, as the $A_{Ac}2$ transition state becomes increasingly less stable because of the insufficient concentration (or activity) of water available to form it and to solvate it. Eventually, a sharp break occurs in the curve, and log $f_{S^{\ddagger}}$ becomes reasonably medium independent. This is reasonable in terms of a changeover in mechanism to an $A_{Ac}1$ process. In this case, the transition state is acylium ion like and is expected to have much less dependence on medium under these strongly ionizing conditions. As this transition state becomes more stable than the A2 transition state, a mechanism change takes place. It is interesting that the acidities at which such mechanistic changeovers occur are very reasonable in terms of the expected order of stabilities of the carbonium-type ions being formed in the rate-determining steps of either $A_{Ac}1$ or $A_{Al}1$ processes. Also, the acidities at which these breaks occur (such as in Figure 5) correspond very closely with the points at which sharp changes are found in various hydration parameter treatments, and which have been used previously to detect mechanism changes.[22]

Other examples of this type of treatment to obtain transition-state activity-coefficient behavior, and hence mechanistic information, will be described in a forthcoming publication. It will be interesting to test the potential utility of this approach on a variety of systems.

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A Sensitive Probe for Double Layer Structure. Potential Dependent Competitive Cyanation and Methoxylation of 1,4-Dimethoxybenzene

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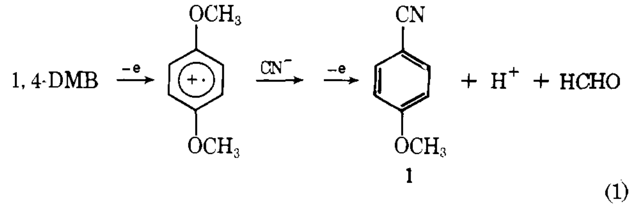
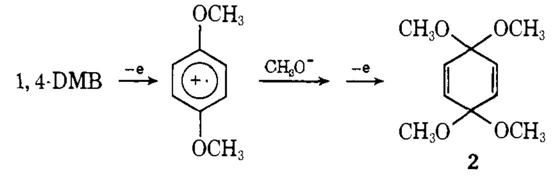
Abstract: It is possible to determine the relative concentrations of nucleophiles at the electrode from products of electrolysis using competitive reactions. The electrochemical oxidation of 1,4-dimethoxybenzene (1,4-DMB) in NaCN-CH_3OH solution affords three primary products, as well as a secondary methanolysis product. The current efficiencies of two products (**1** and **2**) are highly potential dependent, while the current efficiency of the third (**3**) taken together with its methanolysis product (**4**) is found to be independent of potential. Current-potential data support a cation radical mechanism. From the rate expressions it is shown that the concentrations of reactive cationic species formed on electron transfer provide sensitive probes for the relative concentration of nucleophiles (CN^-/CH_3O^-) in the double layer. The dependence of the current efficiencies of **1** and **2** on potential is shown to be related to (CN^-/CH_3O^-) which significantly increases in value as the electrode potential is made positive. In contrast to the above, electrolysis of 1,4-DMB in KOCN-CH_3OH solution provides the quinone diketal (**2**) as the sole aromatic-derived product. The observation is consistent with the order of reactivity of nucleophiles in methanolic solution as $CH_3O^- > CN^- > OCN^- > CH_3OH$.

Among the electrochemical reaction variables[2] requiring considerably more elucidation than is presently available for a detailed understanding of electroorganic synthesis is the role of the electrode potential as it influences both electrochemical adsorption and concentrations of reactive species at the electrode. Certainly studies over the past decade have provided improved models of the region of solution adjacent to the electrode, i.e., the double layer,[3] and increased our knowledge substantially regarding reaction pathways of organic compounds at electrodes.[4-6] Yet most investigations combining organic electrochemistry with an understanding of adsorption processes have dealt with fuel cell-type reactions[7,8] where little can be learned mechanistically from the nature of the simple end products, CO_2 and H_2O. It is a primary purpose of this paper to show that a great deal of insight can be gleaned concerning the potential dependence of concentrations of species at the electrode from the structure and yields of products formed in competitive reactions.

The electrochemical oxidation of 1,4-dimethoxybenzene at a Pt electrode in CH_3CN containing Et_4NCN as supporting electrolyte was shown by Andreades and Zahnow[9] to lead to anisonitrile (**1**) in high yield. Further evidence indicated that the reaction mechanism probably goes through a cation radical route as in eq 1. Likewise, Weinberg and Belleau[10] showed that electrochemical methoxylation of 1,4-DMB in CH_3OH containing KOH as supporting electrolyte gives the quinone diketal (**2**) in about 65% current efficiency (CE). Recently[11] this reaction was shown conclusively to proceed through a cationic route, likely occurring according to eq 2. Consequently, electrooxidation of 1,4-DMB in NaCN-CH_3OH at Pt should afford both of the above products (**1** and **2**) since this electrolyte solution will contain both CN^- and CH_3O^- ions. More importantly, if adsorption processes are involved, it was considered that this system should provide information on the relative (if not absolute) concentration of nucleophiles at the electrode by studying the products (**1** and **2**) as a function of potential.



(1)



(2)

Results

Products. Electrolyses were conducted in 0.5 *M* NaCN-CH_3OH in a three-compartment H-cell in the potential region +1.00 to +1.70 V vs. SCE at Pt electrodes. Four major products were identified by GC and analytical methods in a total of about 100% CE. Besides **1** and **2**, 3-cyano-3,6,6-trimethoxy-1,4-cyclohexadiene (**3**) was found, in addition to some of its methanolysis derivative (**4**). The latter is not a direct electrochemical product but is formed in base catalyzed reaction of **3**.[12] A trace of 4,4-dimethoxy-2,5-cyclohexadienone (**4a**) was also noted. It is of interest that no evidence could be obtained for the presence of the dicyanodiene (**5**) in the reaction product mixture, although this may be a high retention-time product observed in the GC in trace quantity, but not separated.

Products **3** and **4** have not been reported previously, nor was product **5** observed by Andreades and Zahnow[9] in their