Examination of Acidity Functions by Characteristic Vector Analysis †

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Characteristic vector analysis has been applied to 112 acidity function data sets of various strong acids as variables of the percentage, and to 51 acidity function data sets as variables of the molar concentration in water–organic solvents. It has been found that only one characteristic vector, *V*, an independent variable, produces differences in each set of acidity functions. This vector is a statistically universal measure of acidity and depends on acid concentration. It is independent of the nature of the acid. A further parameter, *S*, depends on the nature of the acid and on the acidity function. The reconstituted acidity function given by the equation $H_{m,i} = \bar{H}_{m,i} + V_{1,i}S_{1,m}$ explains more than 98% of the experimental variations of the acidity function.

The acidity function concept was developed by Hammett[1] who defined the acidity function H_0 for sulphuric acid solutions as an extension of the pH scale into the concentrated acid region. It become apparent, however, after experimental work by Arnett[2] and others[3-5] that H_0 was not a unique function but only one of many possible acidity functions. Numerous acidity functions have been developed for water and for water–organic solvents by application of the classical Hammett postulate concerning the activity coefficient term and experimental procedure. The ' failure ' of acidity functions was discussed in terms of indicator structure, hydration phenomena, salt effects,[2] and their influence on the activity coefficient term.

In 1966 Bunnett and Olsen showed that another assumption regarding the activity coefficient term leads to considerable simplification[6] and the number of different acidity functions needed to explain the protonation of different bases has been reduced to one. The linear relations between various acidity functions were presented[7] as an evidence of the validity of the Hammett postulate (or cancellation assumption). The Hammett-type acidity function is still needed and to derive it, two assumptions are involved; these are cancellation and linearity, the latter being more important. This is a method used by Marziano and her co-workers[8] for acid systems and by Cox and his co-workers[9] for basic media. These groups tested the validity of the linearity assumption. Hence the assertion that there is only one acidity function per acid system. New, more general acidity scales were exemplified by M_c[8] and the activity coefficient ' excess ' acidity function X.[10]

A different approach to acidity function ' failure ' was used by Palm and his co-workers.[11] Differences between acidity functions were explained by a four-parameter equation involving polarity, polarizibility, Lewis acidity, and basicity; however the results were far from satisfactory.

This controversy involving the acidity function problem is of essential importance for physical organic chemistry[12] because of the need to study the protonation equilibrium constant, pK_{BH^+} and the relation between reaction rates and medium acidity in acid-catalysed reactions.

This paper attempts a more direct approach to the acidity function problem. This approach is based on characteristic vector analysis (c.v.a.)[13] of existing acidity function data. The power of this approach is that it is not based on a specific theory relating acidity function data to the structure of organic bases and/or type of acid. Rather, the approach is based on a general theory of the behaviour of data observed for similar processes–protonations in strong acid medium. The mathematical theory is in fact an extension of the familiar concept of linear free energy relationship and makes it possible to arrive at reliable conclusions provided the data have been selected in a manner adequate to the problem under study.

Design of the Study.—C.v.a. is a very useful mathematical method to deal with the problem of seeking regularities in chemical or physical data. Recently c.v.a. or a similar approach was used to study intramolecular interactions in the liquid state,[14] kinetic data for solvolytic reactions,[15] extraction of mass spectra from g.l.c.–m.s. data of unseparated mixtures,[16] and protonation phenomena by u.v. spectroscopy.[17]

We have studied processes in the form of acidity function sets as variables of percentage or molarity. Two types of acidity functions are of interest, those established according to the classical procedure[1] and described by equation (1) and those characterizing acids in a simple way (*e.g.* the activity or

$$H = -\log a_{H^+} \cdot \gamma_B/\gamma_{BH^+} \qquad (1)$$

concentration of species existing in acids). All acidity function data were from the literature.

Acidity Functions as Variables of Percentage.—We utilized 41 acidity functions for sulphuric acid, 25 for perchloric acid, 13 for phosphoric acid, eight for nitric acid, seven for hydrochloric acid, six for toluene-*p*-sulphonic acid, and 12 for miscellaneous acids. The types of acidity functions and references are collected in Table 1.

The values of the acidity functions at the required percentages (5% and multiples) were used directly from original source, if available, or were read from the graphs of acidity functions *versus* percentages at desired concentrations.

In spite of employing acid concentration ranges characteristic of particular acids the data matrix was not complete along the concentration axis. The concentration range of hydrochloric acid was 5—37% and after a short extrapolation the last reading was at 40%. Most acidity functions for sulphuric acid cover the range 5—95% but some data were available only in the range up to 40%. A similar situation applies to the remaining acids. Because of the requirements of the c.v.a. method (a complete matrix) the initial incomplete matrix was divided into several submatrices taking the percentage of the acid concentration as the criterion. This division was a compromise between unnecessary omission of existing data, un-

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Table 1. Acidity functions, ranges of acid concentration (%), and values of scalars S_1 and S_2

Acidity function [a]	Concentration range [b]	S_1	S_2	c	Ref.	Acidity function [a]	Concentration range [b]	S_1	S_2	c	Ref.
1 S H_0	xxxxxx	−0.0891	−0.0254	A	18	29 S H_0^1	xxxxxx	−0.3178	−0.1956	A	32
2 S $H_0$25	xxxxxx	−0.0900	0.0258	A	19	30 S H_0^2	xxxxxx	−0.2026	−0.0925	A	32
3 S $H_0$40	xxxxxx	−0.0729	−0.0033	A	19	31 S H_0^3	xxxxxx	−0.0867	−0.0124	A	32
4 S $H_0$60	xxxxxx	−0.0538	0.0077	A	19	32 S H_0^4	xxxx	−0.0602	−0.3782	D	32
5 S $H_0$80	xxxxxx	−0.0415	−0.0162	A	19	33 S H_0DMSO	xxxxxx	−0.2832	0.2438	B	33
6 S $H_0$90	xxxxxx	−0.0264	−0.0353	A	19	34 S H_0'DMSO	xxxxxx	−0.3727	0.0375	B	33
7 S H_R25	xxxxx	−0.4558	0.0918	C	20	35 S $H_0+\lg C_A$	xxxxxx	−0.0248	0.2624	A	34
8 S H_R40	xxxxx	−0.4023	0.0335	C	20	36 S $\lg C_A$	xxxxxx	0.5323	−0.2185	B	34
9 S H_R60	xxxxx	−0.3070	−0.0685	C	20	37 S $\lg a_w$	xxxxxx	0.1719	0.6555	A	35
10 S H_R80	xxxxx	−0.1948	−0.0698	C	20	38 S $\lg C_H$	xxxxxx	0.5275	−0.0299	B	10
11 S H_R90	xxxxx	−0.1395	−0.1165	C	20	39 S $\lg a_H$	xxxx	0.6040	−0.1194	D	36
12 S H_x	xxxxxx	0.6090	−0.5610	A	10	40 S $\lg a_{w+}$	xxxx	0.5387	0.0751	D	36
13 S H_A	xxxxxx	0.1076	−0.3295	B	3	41 S $\lg C_H^*$	xx	0.3581	0.0090	F	37
14 S H_A	xxxxx	0.1392	−0.3925	C	21	42 C H_0	xxx	−0.1756	0.5023	E	38
15 S H_A	x	0.2488	0.0140	G	22	43 C H_R	xx	−0.2564	0.0012	F	39
16 S H'''_0	xxxxxx	−0.2192	−0.0281	B	2	44 C H_x	xxx	0.5934	−0.2452	E	10
17 S H''_0	xxx	−0.1080	−0.0504	E	23	45 C H_A	xxx	−0.0366	−0.1513	E	40
18 S H'_0	xxx	−0.1079	−0.0543	E	23	46 C H_A15	xx	−0.0304	−0.0500	F	41
19 S H'_R	xxxxxx	−0.3798	−0.4401	B	24	47 C H_A25	xx	−0.0392	−0.0524	F	41
20 S H_I	xxx	−0.2409	−0.2015	E	4	48 C H_A35	xx	−0.0281	−0.0566	F	41
21 S H_M	xxx	−0.2816	−0.3661	E	25	49 C H_A45	xx	−0.0267	−0.0633	F	41
22 S H_c	xxxx	−0.3281	−0.4775	D	26	50 C H'''_0	xxx	−0.3428	0.4210	E	40
23 S M_c	xxxxxx	0.2570	−0.0102	A	27	51 C H_I	x	0.604	0.2348	C	4
24 S H_{GF}	xx	−0.1443	0.0342	F	28	52 C H_M	xx	−0.1987	0.0799	F	42
25 S H^+	xxx	−0.0988	−0.3478	E	29	53 C H_c	xx	−0.1772	0.1315	F	26
26 S H_T	xxxx	−0.2667	−0.3664	D	30	54 C Δ	xx	0.1577	0.0251	F	21
27 S Δ	xxxxxx	0.4088	0.0682	A	31	55 C H_0^0	xx	−0.2432	0.0626	F	32
28 S H_0^0	xxxxxx	−0.4352	−0.2991	A	32	56 C H_0^1	xx	−0.1825	0.0660	F	32

Acidity function [a]	Concentration range [b]	S_1	S_2	c	Ref.	Acidity function [a]	Concentration range [b]	S_1	S_2	c	Ref.
57 C H_0^2	xx	−0.1219	0.0587	F	32	85 TS H_{GF}	xx	0.0513	0.1703	F	46
58 C H_0^3	xx	−0.0611	0.0587	F	32	86 TS lg C_H^*	xx	0.2112	0.2514	F	46
59 C H_0^4	xx	0.0003	0.0600	F	32	87 N H_0	x	0.2640	−0.1794	G	39
60 C H_0^5	xx	0.0603	0.0561	F	32	88 N H_R	xx	−0.2072	−0.3304	F	39
61 C D_0	xx	−0.0832	0.0996	F	43	89 N Δ	xx	0.1466	0.0491	F	32
62 C D_x	xx	−0.0410	0.1317	F	43	90 N H_0^0	xx	−0.2072	−0.3305	F	32
63 C H'_0EtOH	x	0.1311	0.7753	G	44	91 N H_0^1	xx	−0.1646	−0.1896	F	32
64 C $\lg C_H$	xxx	0.3373	0.4625	E	10	92 N H_0^2	xx	−0.0989	−0.2403	F	32
65 C $\lg a_H$	xx	0.4083	−0.0801	F	36	93 N H_0^3	xx	−0.0440	−0.1935	F	32
66 C $\lg a_{W+}$	xx	0.1119	−0.0497	F	36	94 N H_0^4	xx	0.0095	−0.1492	F	32
67 P H_R	xxxx	−0.1727	0.2709	D	2	95 Cl H_0	x	−0.0503	0.1718	G	45
68 P H'''_0	xxxx	−0.0599	0.0976	D	2	96 Cl H_R	x	−0.5066	0.0688	G	46
69 P H'_0	xxxx	0.0241	0.1446	D	2	97 Cl H_A	x	0.0012	−0.3119	G	47
70 P H'_R	xxxx	−0.1308	0.2053	D	2	98 Cl H'_0	x	−0.0544	−0.1078	G	2
71 P H_{GF}	xxxx	−0.1203	0.1529	D	37	99 Cl H'''_0	x	−0.2519	−0.2967	G	2
72 P $\lg C_H^*$	xx	0.2407	−0.1435	F	37	100 Cl H'_R	x	−0.4259	−0.1034	G	2
73 P $H'_0+\lg a_{H+}$	xx	0.1978	0.1237	F	—	101 Cl Δ	x	0.5836	−0.2635	G	31
74 P Δ	xxxx	0.1989	−0.3898	D	32	102 F H_0	xx	−0.0612	0.4491	F	48
75 P H_0^0	xxxx	−0.1729	0.2759	D	32	103 F Δ	xx	0.1436	−0.1078	F	49
76 P H_0^1	xxxx	−0.1070	0.2049	D	32	104 F H_0^3	xx	−0.0612	0.3923	F	49
77 P H_0^2	xxxx	−0.0414	0.1520	D	32	105 MS $\lg C_H^*$	xx	0.2408	0.0685	F	37
78 P H_0^3	xxxx	0.0243	0.1043	D	32	106 MS H_{GF}	xxxxx	0.0694	−0.1279	C	37
79 P H_0^4	xxxx	0.0902	0.0475	D	32	107 CF_3 H_{GF}	xxxxxx	0.0954	0.7626	B	38
80 HP $\lg C_{H+}$	xxx	0.4629	0.0667	E	37	108 SE H_0	xxxxxx	0.0058	0.2066	A	49
81 TS	xx	0.0595	0.1126	F	2	109 HC Δ	xxxxx	0.4673	−0.5570	C	32
82 TS H_R	xx	0.0042	−0.0385	F	2	110 HC H_0^0	xxxxx	0.2030	0.4228	C	32
83 TS H'''_0	xx	0.0589	0.1490	F	2	111 HC H_0^1	xxxxx	0.2744	0.4039	C	32
84 TS H_R	xx	0.0079	−0.0450	F	2	112 HC H_0	xxxxx	0.3548	0.3804	C	32

[a] S, Sulphuric acid; C, perchloric acid; P, phosphoric acid; HP, phosphonic acid; TS, toluene-*p*-sulphonic acid; N, nitric acid; Cl, hydrochloric acid; B, hydrobromic acid; J, iodic acid; F, hydrofluoric acid; MS, methane sulphonic acid; FS, fluorosulphonic acid; CF_3 trifluoroacetic acid; SE, selenic acid; HC, formic acid; Et, ethanol; DX, dioxan; Be, 2-butoxyethanol; AN, acetonitrile. [b] x, 40%; xx, 55%; xxx, 70%; xxxx, 80%, xxxxx, 90%; xxxxxx, 95%. [c] Submatrix A—G.

necessary extrapolation of non-existing data, and dealing with a reasonably small number of submatrices. Only in a very few cases was extrapolation done over a range of <3%, and only few data were neglected.

The following ranges of acid concentration were examined, 5—40, 5—55, 5—70, 5—80, 5—90, and 5—95%, and are indicated in Table 1 for each acidity function by G, F, E, D, C, and A/B, respectively.

Table 2. Results of c.v.a. calculation for submatrices A—G (percentage mode)

Sub-matrix	%Total variation				Concentration (%)									
	V_1	$V_1 + V_2$	N[a]		5	10	15	20	25	30	35	40	45	50
95% A	99.82	99.98	16	V_1	0.066	0.927	1.723	2.543	3.399	4.301	5.311	6.371	7.510	8.788
				V_2	−0.042	0.138	0.288	0.391	0.494	0.572	0.683	0.766	0.813	0.858
				$-\bar{H}$	0.059	−0.250	0.509	0.774	1.029	1.293	1.564	1.854	2.176	2.545
95% B	99.22	99.85	8	V_1	−0.229	0.867	1.668	2.411	3.137	3.842	4.608	5.475	6.437	7.403
				V_2	0.723	0.737	0.724	0.747	0.755	0.789	0.808	0.793	0.714	0.640
				$-\bar{H}$	−0.123	0.233	0.532	0.817	1.108	1.403	1.732	2.113	2.542	2.982
90% C	98.94	99.83	11	V_1	1.302	1.756	2.533	3.141	2.843	4.645	5.453	6.448	7.483	8.504
				V_2	1.790	1.766	1.653	1.513	1.331	1.213	0.983	0.763	0.767	0.357
				$-\bar{H}$	−0.527	−0.201	0.193	0.502	0.884	1.285	1.664	2.093	2.575	3.061
80% D	99.57	99.93	16	V_1	−1.016	0.335	1.662	2.877	4.149	5.445	6.822	8.406	10.18	12.02
				V_2	1.468	1.337	1.159	1.003	0.873	0.716	0.589	0.547	0.519	0.468
				$-\bar{H}$	−0.607	−0.377	−0.165	0.058	0.272	0.480	0.689	0.903	1.149	1.428
70% E	99.26	99.94	11	V_1	−0.271	0.837	1.742	2.565	3.357	4.264	5.259	6.408	7.641	8.680
				V_2	−0.146	0.193	0.405	0.540	0.671	0.710	0.788	0.860	0.866	0.787
				$-\bar{H}$	0.012	0.300	0.536	0.749	0.968	1.187	1.432	1.705	1.996	2.285
55% F	98.82	99.83	39	V_1	0.130	2.641	4.929	6.963	8.951	11.05	13.37	16.05	19.02	22.45
				V_2	1.642	1.611	1.582	1.565	1.538	1.475	1.271	0.818	0.037	−1.102
				$-\bar{H}$	−0.011	0.244	0.458	0.654	0.849	1.045	1.245	1.479	1.742	2.061
40% G	99.42	99.82	11	$V]$		1.890	2.818	3.852	5.026	6.294	7.495	8.719		
				V_2		0.601	0.600	0.352	0.243	0.003	−0.192	−0.453		
				$-\bar{H}$		0.844	1.344	1.896	2.441	3.040	3.637	4.213		

Sub-matrix	% Total variation				Concentration (%)								
	V_1	$V_1 + V_2$	N[a]		55	60	65	70	75	80	85	90	95
95% A	99.82	99.98	16	V_1	10.21	11.84	13.63	15.47	17.42	19.35	21.47	23.39	25.50
				V_2	0.903	0.960	0.946	0.785	0.468	−0.020	−0.440	−1.046	−1.862
				$-\bar{H}$	2.949	3.410	3.931	4.474	5.068	5.647	6.284	6.862	7.568
95% B	99.22	99.85	8	V_1	8.363	9.518	10.81	12.05	13.13	14.04	15.26	16.03	16.64
				V_2	0.594	0.616	0.524	0.459	0.295	0.157	−0.590	−1.176	−1.595
				$-\bar{H}$	3.429	3.968	4.557	5.158	5.718	8.242	8.969	7.578	8.123
90% C	98.94	99.83	11	V_1	9.797	11.25	12.47	14.06	15.48	16.44	17.62	18.74	
				V_2	0.195	0.060	−0.067	−0.193	−0.312	−0.466	−0.717	−0.882	
				$-\bar{H}$	3.608	4.223	4.888	5.523	6.208	6.808	7.498	8.239	
80% D	99.57	99.93	16	V_1	13.85	15.82	17.91	20.26	22.25	24.92			
				V_2	0.385	0.220	−0.136	−0.291	−0.511	−0.809			
				$-\bar{H}$	1.708	2.024	2.386	2.765	3.213	3.621			
70% E	99.26	99.94	11	V_1	10.57	12.42	14.52	16.79					
				V_2	0.437	−0.081	−0.742	−1.416					
				$-\bar{H}$	2.657	3.075	3.537	4.0494					
55% F	98.82	99.83	39	V_1	26.60								
				V_2	−2.231								
				$-\bar{H}$	2.454								
40% G	99.42	99.82	11	V_1									
				V_2									
				$-\bar{H}$									

[a] Number of acidity functions.

Acidity Functions as Variable of Molarity.—We utilize 24 acidity functions for sulphuric, perchloric, and hydrochloric acids in water–organic solvents. In addition six acidity functions for less popular acids were studied. In all cases there were no data available for conversion of the molar concentrations into percentages. We also included 21 of the most important acidity functions for sulphuric, perchloric, and hydrochloric acids in water.

A types of acidity functions and references to the original source were collected in Table 2, together with molarity range. An initial and incomplete data matrix was divided into several submatrices taking molarity of acids as criterion. The following

Table 3. Acidity functions, ranges of molar concentration, and values of S_1 and S_2

	Acidity function	Concentration range [b]	$S_{m,1}$	$S_{m,2}$	*c*	Ref.	$S_{m,1}$4M
1	S H_0	xxxxx	−0.0474	−0.1279	H	18	−0.0471
2	S H_0Et20%	xxxxx	−0.0863	0.0452	H	50	−0.0416
3	S H_0Et20%	xxxxx	−0.0838	0.0193	H	51	−0.0522
4	S H'Et20%	xxxxx	−0.1655	0.0423	H	52	−0.0942
5	S H_0Et50%	xxxx	−0.1449	−0.1801	I	53	−0.1242
6	S H_R	xxxxx	−0.2808	−0.0012	H	20	−0.1675
7	S $^0H_0$	xxxxx	−0.2570	−0.1382	H	47	
8	S $^0H_0$Et20%	xxxxx	−0.3366	0.0359	H	47	−0.2095
9	S H_{GF}	xxxxx	−0.1772	−0.1264	H	28	−0.1261
10	S H_{GF}Et20%	xxxxx	−0.1217	0.7911	H	28	0.0433
11	S H_{GF}DX40%	xxxx	−0.0714	0.8785	I	28	0.0184
12	S H_{GF}DX60%	xxx	−0.8001	0.1627	K	28	0.0853
13	S H_{GF}AN75%	xx	−0.4296	0.4506	L	28	
14	S Δ	xxxxx	0.2418	−0.0019	H	31	0.1568
15	S Δ Et20%	xxxxx	0.2538	−0.0159	H	47	0.1636
16	S lga_H	xxxxx	0.5588	0.1173	H	37	0.3752
17	S M_c	xxxxxx	−0.0038	0.0837	H	27	0.0087
18	S H_x	xxxx	0.3219	−0.0324	H	10	0.2027
19	S H_A	xxxxx	0.0072	−0.2435	H	3	−0.0275
20	S H_+	xxxxx	−0.0499	−0.2509	H	29	−0.0663
21	C H_0	xxxxx	−0.0748	0.0734	H	38	
22	C H_0Et50%	xxxx	−0.1184	−0.0044	I	54	−0.1004
23	C H_0'DX40%	xx	0.0829	0.0903	L	55	−0.0012
24	C H'_0DX60%	xx	0.0557	0.2859	L	55	−0.0087
25	C $^3H_0$	xxxx	−0.0014	−0.1149	I	47	−0.0383
26	C $^3H_0$Be40%	xx	0.1180	0.2248	L	47	0.0202
27	C $^3H_0$Be60%	xx	0.0901	0.3221	L	55	0.0094
28	C H_R	xxxx	−0.3258	−0.3704	I	56	0.2507
29	C H_RDX40%	xx	−0.3591	−0.5171	L	57	−0.2381
30	CH_RDX60%	xx	−0.4791	−0.3493	L	57	−0.2923
31	C Δ	xxxx	0.3646	−0.0299	I	31	0.1822
32	C Δ DX40%	xx	0.4424	−0.1229	L	47	0.1700
33	C Δ DX60%	xx	0.4788	−0.3851	L	47	0.1800
34	C H_{GF}	xx	−0.1807	−0.0827	L	28	−0.1381
35	C lga_H	xx	0.7801	−0.0768	L	37	0.4172
36	C M_c	xxxxx	−0.0265	0.2998	H	27	0.0156
37	Cl H_0	xxxxx	0.0061	−0.1246	H	45	−0.0101
38	Cl H_0Et50%	xxxx	−0.0227	−0.1354	I	54	−0.0557
39	Cl H_0AN10%	x	−0.8124	−0.0916	M	58	
40	Cl H_0AN30%	x	−0.1667	0.2748	M	58	
41	Cl H_0AN50%	x	0.2947	0.5431	M	58	
42	Cl H_0AN80%	x	0.0252	0.0026	M	58	
43	Cl H_R	xxxxx	−0.1280	−0.1267	H	2	−0.0955
44	Cl H_A	xxxxx	0.0172	−0.1581	H	45	−0.0087
45	Cl Δ	xxxxx	0.1945	−0.0593	H	31	0.1195
46	B $^3H_0$	xxxxx	0.0185	−0.1273	H	59	−0.0043
47	B Δ	xxxxx	0.2203	0.0407	H	47	0.1503
48	J $^3H_0$	xxx	0.2591	−0.7743	K	60	0.0727
49	J Δ	xxx	0.5409	0.6116	K	47	0.1253
50	FS H_{GF}	xxxx	−0.2781	0.1160	I	61	−0.1528
51	CF$_3$ H_{GF}	xxxx	0.0189	0.3949	I	61	0.0482

[a] See footnotes to Table 1. [b] x, 2.5M; xx, 4.0M; xxx, 5.5M; xxxx, 7.0M; xxxxx, 10.0M. [c] Submatrices H—M.

ranges of acid concentration have been used, 2.5, 4.0, 5.5, 7.0, and 10.0M in 0.5M intervals and are indicated in Table 3 for each acidity function by M, L, K, I, and H, respectively.

Mathematical Description of C.v.a.—C.v.a.[13] can be used to estimate the number of independent orthogonal vectors contributing to the total variation observed in the data set. In the case of values of H_i taken at n concentrations, $i = 1,2 \dots n$ constitute one row of an n-column data vector. For m acidity functions the m vectors can be arranged to form an $m \,.\, n$ data matrix. The characteristic vectors $V_{m,i}$ are uniquely determined for a matrix of acidity functions and apply to all data vectors. Characterisitc vectors form a set of $i = 1,2 \dots n$ numbers.

Acidity function may be represented by equation (2) where

$$H_{m,i} = \bar{H}_{m,i} + S_{m,1}V_{1,i} + S_{m,2}V_{2,i} + \dots + S_{m,k}V_{k,i} \tag{2}$$

the S values are the amounts of the characteristic vectors which must be added to the mean acidity function vector $\bar{H}_{m,i}$ in order to obtain the sample vector. The parameter S is specific to the acidity function. The number of characteristic vectors required to represent all the variation among the data set will be equal to or less than n and in general is much less than n. The number of characteristic vectors is smaller, the closer the

Table 4. Results of c.v.a. calculation for submatrices H–M (concentration mode)

Sub-matrix	% Total variation V_1	$V_1 + V_2$	N[a]		Concentration (mol) 0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
10.M H	99.07	99.87	24	V_1	−0.206	1.104	2.347	3.419	4.507	5.551	6.594	7.702	8.878
				V_2	0.415	0.729	1.049	1.237	1.284	1.309	1 289	1.216	1.150
				$-\bar{H}$	−0.108	0.191	0.401	0.590	0.777	0.954	1 128	1.318	1.505
7.0M I	98.28	99.75	8	V_1	−0.146	1.223	2.269	3.143	4.013	4.954	5.948	6.900	7.877
				V_2	1.756	1.488	1.329	1.344	1.117	0.926	0.677	0.407	0.187
				$-\bar{H}$	−0.234	0.168	0.435	0.672	0.905	1.157	1.456	1.735	2.004
5.5M K	98.03	99.99	3	V_1	−2.267	−1.794	−1.292	−0.844	−0.456	0.012	0.684	1.366	2.017
				V_2	0.095	0.235	0.279	0.306	0.338	0.344	0.303	0.242	0.167
				$-\bar{H}$	−1.143	−0.827	−0.551	−0.325	−0.130	0.097	0.402	0.707	0.993
4.0M L	93.42	99.56	11	V_1	−1.924	−0.164	1.017	2.173	3.262	4.355	5.424	6.507	
				V_2	1.838	1.288	1.085	0.812	0.511	0.267	−0.035	−0.271	
				$-\bar{H}$	−0.861	−0.403	0.082	0.533	0.963	1.383	1.812	2.221	
2.5M M	70.35	98.20	4	V_1	0.782	0.661	0.470	0.228	−0.036				
				V_2	−0.130	−0.044	0.146	0.368	0.589				
				$-\bar{H}$	−1.035	−0.530	−0.133	0.207	0.517				

Sub-matrix	% Total variation V_1	$V_1 + V_2$	N[a]		Concentration (mol) 5.0	5.5	6.0	6.5	7.0	7.5	8.0	9.0	10.0
10.0M H	99.07	99.87	24	V_1	10.06	11.30	12.55	13.76	15.06	16.39	17.69	20.45	23.37
				V_2	1.053	0.989	0.775	0.493	0.217	−0.120	−0.505	−1.318	−2.225
				$-\bar{H}$	1.718	1.896	2.112	2.322	2.543	2.769	2.995	3.488	4.002
7.0M I	98.28	99.75	8	V_1	8.992	10.06	11.18	12.60	13.91				
				V_2	0.044	−0.214	−0.490	−0.660	−0.765				
				$-\bar{H}$	2.273	2.549	2.843	3.252	3.570				
5.5M K	98.03	99.99	3	V_1	2.556	3.024							
				V_2	0.115	0.078							
				$-\bar{H}$	1.233	1.443							
4.0M L	93.42	99.56	11	V_1									
				V_2									
				$-\bar{H}$									
2.5M M	70.35	98.20	4	V_1									
				V_2									
				$-\bar{H}$									

[a] Number of acidity functions.

similarity between the acidity functions. The importance of a particular vector is measured as percentage of the total variability, %TV, explained by this vector.

A mathematical method for estimating the number of characteristic vectors and their values has been developed for complete matrices only. The method allows us to calculate the first reconstituted data matrix using only the first characteristic vector $V_{1,i}$ and the percentage of total variability of the original data described by this matrix. The calculation is continued until the percentage of total variability reaches 100% or with the desired and declared number of characteristic vectors.

The mathematical model described by equation (2) is seen to have the multiparameter form of a linear free energy relationship (l.f.e.r.) and should be valid for the following conditions; (1) the acidity function (index m) has some degree of similarity, (2) the variables of concentration are related to this similarity and have continuous properties in the range $i = 1,2 \ldots n$. Both conditions are well fulfilled in acidity function data set.

Results and Discussion

Tables 1—4 present the most significant results of the c.v.a. calculation for 142 acidity functions of 15 strong acids as variables of percentage and molarity divided into 12 submatrices. Acidity functions available for the 95% parameters are grouped into two submatrices A and B because of much better results for separate treatments. The number of acidity functions in each submatrix is given by N; the acid and acidity function used in each submatrix can be found from the data in columns 2 and 5 of Tables 1 and 3.

One variable suffices to explain >98% of the variance for several acidity functions and acids of various chemical properties, except submatrices L and M. An increase in the number of variables to two will improve this explanation to

Table 5. Parameters of linear and/or potential regression of $V_{1,t}$ and ranges of acid concentration

	5—35% or 0.5—5.0M				40—95% or 6—10M			
Submatrix	$V_1 = bC + a$	r	s	n	$V_1 = aC^b$	r	s	n
A	$0.1726\,C - 0.8419$	0.9986	0.0331	7	$0.0148\,C^{1.6361}$	0.9992	0.0773	12
B	$0.1566\,C - 0.8036$	0.9951	0.0529	7	$0.0413\,C^{1.3282}$	0.9963	0.1021	12
C	$0.1396\,C + 0.4473$	0.9952	0.0495	7	$0.0431\,C^{1.3570}$	0.9971	0.1320	11
D	$0.2587\,C + 2.2788$	0.9998	0.0131	7	$0.0274\,C^{1.5540}$	0.9998	0.0517	9
E	$0.1790\,C - 1.0436$	0.9998	0.0342	7	$0.0103\,C^{1.7347}$	0.9934	0.1328	7
F	$0.4326\,C - 1.7906$	0.9988	0.0733	7	$0.0466\,C^{1.5815}$	0.9979	0.0406	4
G	$0.2265\,C - 0.5327$	0.9970	0.0435	7				
H	$2.2517\text{M} - 1.2503$	0.9992	0.0548	13	$1.3739\text{M}^{1.2298}$	0.9999	0.0136	5
I	$1.8677\text{M} - 0.6170$	0.9885	0.0572	10				
K	$1.0990\text{M} - 3.0428$	0.9936	0.0715	10				
L	$2.2114\text{M} - 2.3057$	0.9997	0.0237	8				
M	$-0.4124\text{M} + 1.0394$	0.9803	0.0126	5				

r, Correlation coefficient; s, standard deviation; n, number of observations; C, percentage; M molarity.

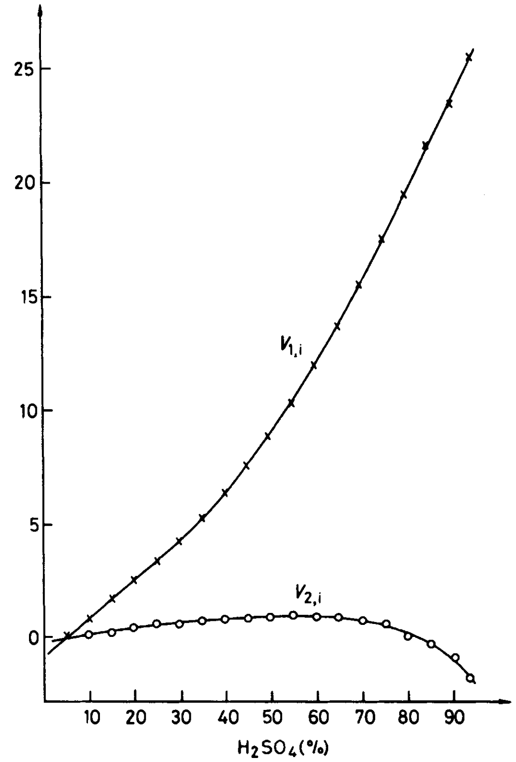

Figure 1. Plot of characteristic vectors V_2 against V_1 for submatrix A as a function of concentration

Table 6. Linear regression equations for V_1 characteristic vectors

Regression equation	r	s	n
$V_B = 0.9107V_A + 0.6736$	0.9865	0.1214	19
$V_C = 0.7824V_A + 1.4087$	0.9944	0.1440	18
$V_D = 1.3393V_A - 0.4183$	0.9971	0.0469	16
$V_E = 1.0817V_A - 0.3451$	0.9983	0.0935	14
$V_F = 2.5381V_A + 0.2138$	0.9989	0.1099	11
$V_G = 1.2911V_A + 0.6100$	0.9991	0.0432	7
$V_I = 0.8771V_H + 0.1176$	0.9997	0.0347	12
$V_K = 0.4785V_H - 2.3381$	0.9972	0.0469	11
$V_L = 1.0488V_H - 1.3196$	0.9998	0.0155	7
$V_M = -0.1747V_H + 0.8114$	0.9664	0.0188	5

$>99.5\%$ of the experimental variance in the data set except for submatrix M. The very low result for submatrix M is associated with random scattering, poor representation of the acidity functions, and very narrow concentration range (2.5M-hydrochloric acid is *ca.* 10%). The submatrix M is intermediate between the lower and higher concentration ranges.

The ' characteristic vectors ' $V_{1,t}$ and $V_{2,t}$ are the only significant eigenvalues. Their values were presented in Tables 2 and 4 for all submatrices as a function of concentration. $V_{1,t}$ and $V_{2,t}$ are presented by Figure 1 for submatrix A. The shape of $V_{1,t}$ is in general similar to the graph of acidity function *versus* percentage of acid concentration. The shape of all $V_{1,j}$ vectors (submatrices B—L) are very similar and consist of two parts, linear in the low concentration range (5—35% and 0.5—5.0M) and curved at higher concentrations. The curved part of the graph can be represented by equation (3)

$$V_{1,t} = aC^b \qquad (3)$$

where a and b represent regression parameters and C is the concentration. The parameters for linear and potential regression are presented in Table 5.

The first characteristic vectors $V_{1,t}$ calculated for various submatrices are linearly related to each other. The $V_{1,t}$ for submatrices A (percentage mode) and H (molarity mode) were chosen arbitrarily as typical values for submatrices B—G and I—M, respectively, and regression parameters are shown in Table 6. As a rule, the correlation coefficients are very high in all cases.

Regression parameters between V_A and some acidity functions for sulphuric acid are given in Table 7 and show a good linear relation. A very good linear relation also exists between log $a_{H^+}{}^*$, the proton activities of various acids, as indicated by the data in Table 7. In the literature log $a_{H^+}{}^*$ is considered to be a better operational scale of acidity in concentrated acids [18] than any other acidity function thus far used.

A two-term equation (4) has been found for describing the various acidity functions in organic and inorganic acids using

$$H_{m,t} = \bar{H}_{m,t} + V_{1,t}S_{m,t} + V_{2,t}S_{m,2} \qquad (4)$$

numerical values from Tables 1—4. The last term in equation (4) could be neglected in acidity function reconstitution if its value does not exceed the experimental error, normally ±0.05

Table 7. Linear regression equation between various acidity functions and reference value V_A

$$
\begin{aligned}
\text{S } H_0 &= -0.3806V_A + 0.0041 & r\ 0.9995\\
\text{S } H_x &= 0.3432V_A - 0.4353 & r\ 0.9862\\
\text{S } H_{MC} &= -0.3656V_A + 0.0167 & r\ 0.9946\\
\text{S } 1gC_{H^+} &= 0.5308V_A + 0.4588 & r\ 0.9594\\
\text{S } 1ga_{H^+} &= 0.6742V_A + 0.0612 & r\ 0.9994\\
\text{C } 1ga_{H^+} &= 0.8159V_A - 0.1700 & r\ 0.9972\\
\text{P } 1ga_{H^+} &= 0.4609V_A - 0.5368 & r\ 0.9758\\
\text{HP } 1ga_{H^+} &= 0.2450V_A - 0.2519 & r\ 0.9929\\
\text{TS } 1ga_{H^+} &= 0.3963V_A - 0.5884 & r\ 0.9797\\
\text{MS } 1ga_{H^+} &= 0.3523V_A + 0.1835 & r\ 0.9990
\end{aligned}
$$

unit. The magnitude of $V_{2,t}$ is not very large and in most submatrices at low concentration is constant or growing slowly; at higher concentration the magnitude of $V_{2,t}$ is increasing and in few cases is less than -1.5.

In our opinion $V_{2,t}$ is associated with failure of acidity function determination procedure and experimental errors. In the method used, ionization ratios are not always perfectly linear and parallel and introduce cumulative errors of uncertain magnitude.[37] Multiplication of $V_{2,t}$ by $S_{2,m}$ yield the contribution of all errors to the acidity function. This contribution depends on concentration and could be neglected under condition $V_{2,t}S_{m,2} < 0.05$. Thus equation (5) simplifies to a one-parameter equation. Consequently there appears to be no more than one type of variable which produce a significant and truly independent difference in the acidity function data set. In other words, any theory of acidity functions which explains these properties in terms of more than one adjustable parameter seems likely to contain redundant information. The existence of only one significant characteristic vector indicates the close similarity between acidity functions in all submatrices. The reconstituted acidity function set using the parameters of equation (5) will be the best and will be error free.

$$H_{m,t} = \bar{H}_{m,t} + V_{1,t}S_{m,2} \qquad (5)$$

The question arises: what is a chemical significance of $V_{1,t}$ and $S_{m,1}$? The specific pattern of $V_{1,t}$ in all submatrices, the possibility of a mathematical description (see Table 5) as a function of concentration, the linear relation for all $V_{1,t}$ values in submatrices A—G and H—L, and the independence of the nature of the acid lead to the conclusion that the first characteristic vector is itself a statistically universal measure of acidity. The numerical values of $V_{1,t}$ are not fixed because they depend on the initial data set. $V_{1,t}$ calculated for the concentration range 5—95% (submatrix A) was chosen arbitrarily as the reference variable for all submatrices in the percentage mode. Its numerical values can be used as the universal acidity measure instead of M_c,[8] X,[10] or log a_{H^+}*.[37] The advantage of $V_{1,A}$ and $V_{1,H}$ is their independence of the nature of the acid. They depend on the concentration, however.

The rationalization of $S_{m,1}$ and $S_{m,2}$ values with respect to a particular type of acidity function (*e.g.* H_0, H_R, H_A), acid, and concentration is very difficult due to the fact that these parameters were calculated for separate submatrices. However some existing trends are in good agreements with the results of another approach. That approach was derived from the results of calculations in which 112 or 102 acidity functions were used in acidity ranges 5—40 or 5—55%, respectively. The S_1–S_2 relation for all acids and the 102 acidity functions is presented in Figure 2.

The points for perchloric and sulphuric acids are widely distributed along the S_1 axis together with the narrow distribution along the S_2 axis (+0.05 and −0.06). The similar data for hydrochloric acid (in the acidity range 5—40%) are distributed in a similar way along the S_1 axis and in the −0.08 to −0.12 range of the S_2 axis. Data for nitric acid are scanty and are distributed below these for other strong acids; they yield a linear relationship of positive slope. The picture is similar for phosphoric acid; however S_2 values are positive and the slope is negative. Points for toluene-*p*-sulphonic acid are widely distributed along the S_2 axis together with a narrow distribution along the S_1 axis. Points for other acids are very limited. Data for selenic acid and methanesulphonic acid fall in the area for sulphuric acid. Data for hydrofluoric acid, trifluoroacetic acid, and phosphonic acid overlap with those for phosphoric acid.

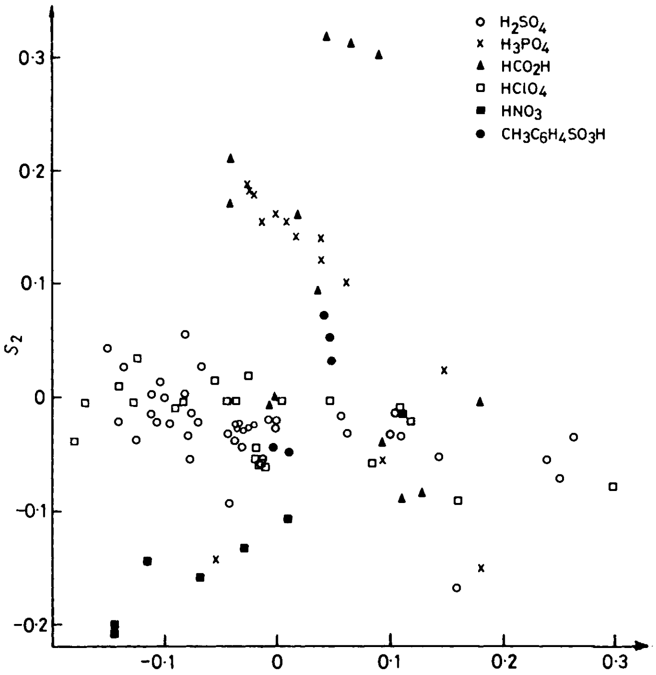

Figure 2. Plot of S_2 against S_1 for 102 acidity functions in the 5—55% concentration range

Careful inspection of the $S_{1,m}$ data for sulphuric acid from the set of 102 acidity functions in the concentration range 5—55% leads to the conclusion that numerous acidity functions have identical figures. For example $H_0{}^3$, H'_0, and H'''_0 have $S_{1,m}$ −0.036 and H_I and H_T have $S_{1,m}$ −0.079. Frequently $S_{1,m}$ values for various acidity functions are very close to each other, *e.g.* Δ and log C_H, $H_0{}^3$ and H_0, H_{GF} and H_C. The conclusion is that these acidity functions have much the same nature and follow the cancellation assumption.[19] Thus the number of original acidity functions could be reduced, though not to five as suggested by Carpentier.[61]

Similar trends could be observed for the $S_{m,1}$ and $S_{m,2}$ data for acidity functions in water–organic mixtures as variables of the molar concentration. That approach was derived as a result of calculating all existing data in the concentration range 0.5—4.0M. The S_1–S_2 relationship for 44 acidity functions as variables of the molar concentration is presented by Figure 3.

Points are distributed mainly along the S_1 axis together with a narrow distribution along the S_2 axis. Limited numbers of points strongly deviating along the S_2 axis represent acidity functions in mixed solvents, water–dioxan, water–2-butoxyethanol, and ocasionally water–ethanol. The number of data is not very large, however; Figure 4 shows the relation be-

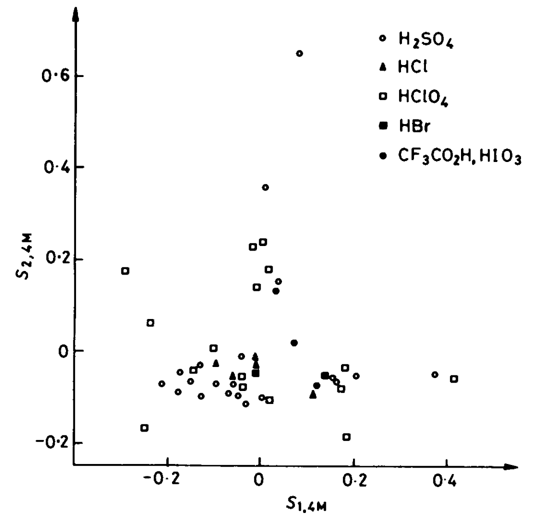

Figure 3. Plot of S_2 against S_1 for acidity functions in 0.5—4.0M concentration range

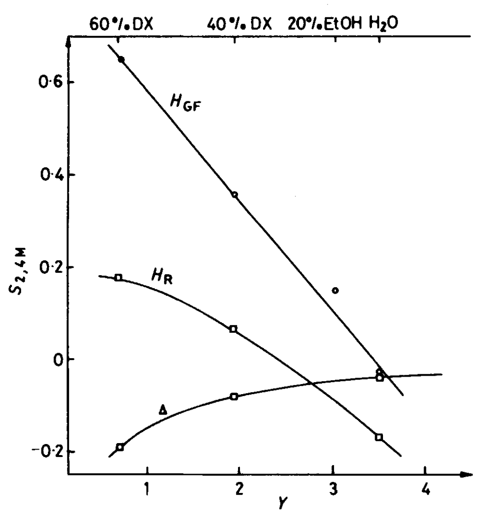

Figure 4. S_2 values for selected acidity functions in water–organic solvents as a function of solvent parameter Y

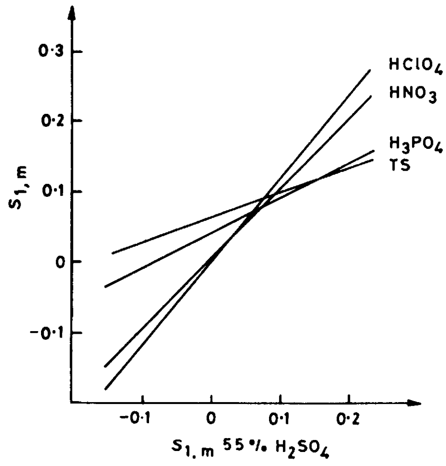

Figure 5. Plot of $S_{m,1}$ for various acids and acidity functions in the 5—55% concentration range against $S_{m,1}$ for sulphuric acid as reference parameter (percentage mode)

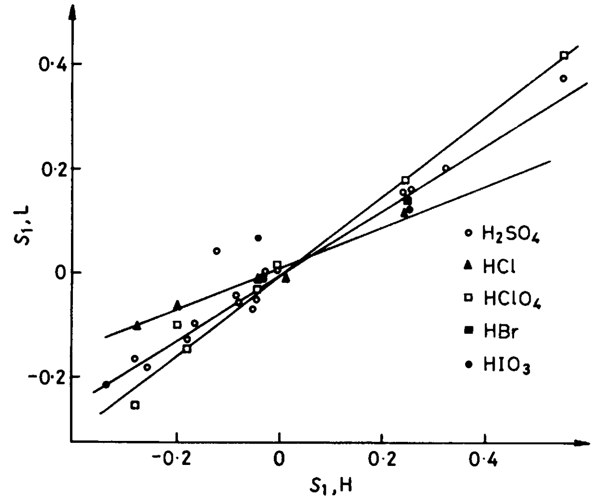

Figure 6. Plot of $S_{m,1}$ for various acids and acidity functions in the concentration range 0.5—4.0M against $S_{m,1}$ for sulphuric acid as reference parameter (concentration mode) (see Table 4 for H and L)

tween $S_{m,2}$ and the polarity of solvents as measured by the Y parameter.[62] The relationship is not very far from linear.

The importance of $S_{m,2}$ is not very large due to the small value of $V_{2,i}$. However in the H_{GF} acidity function in sulphuric acid and the H_R and δ acidity functions in perchloric acid, the contribution of $S_{m,2}V_{2,i}$ is significant and depends on the polarity.

A linear relation of $S_{m,1}$ for various acids with $S_{m,1}$ for sulphuric acid as reference parameter suggests that the nature of acidity functions of identical type is independent of the acid, and activity coefficient terms are related to each other. The proportionality factor is simply the slope of the lines in Figures 5 and 6. This slope reflects the nature of the acid and the decrease in pK_a of acids in a qualitative way. It is desirable to focus attention on this problem in future. A slope >1 indicate a stronger acid than sulphuric or that the numerical value of the desired acidity function at the same concentration is more negative than in sulphuric acid. A slope <1 indicates the opposite.

The results of our method can be used for prediction purposes. First, the data collected in Tables 1—4 are sufficient to provide the best values of any acidity function used in calculations. Also, an unknown acidity function could be predicted for any acid studied with the condition, however, that the relationship of $S_{m,1}$ and $S_{m,1}$ (for sulphuric acid as reference parameter) is defined. Thus new acidity functions for hydrochloric, nitric, methanesulphonic, and phosphoric acids are accessible.

The application of the statistically universal measure of acidity, $V_{1,i}$ to protonation phenomena and kinetic problems in acid catalysed reactions will be discussed in future papers.

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