

THE RANGE OF VALIDITY AND THE PRECISION OF A CORRELATION EQUATION

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Statistical characteristics were calculated for three relationships involving the direct correlation of two experimental quantities (models 1–3, Table I). Their range of validity was systematically explored, including the range of the original Hammett and Taft equations, and their modifications, extensions, and combinations. An optimum range of validity with the highest precision — expressed by the statistic ψ or by the correlation coefficient r — exists in each case, while the precision drops when this range is either too extended or too narrow. This result agrees with intuition and is believed to be of general validity. This analysis revealed also the individual structural factors affecting the precision of the correlations most markedly, but most of them (*e.g.* the *ortho* effects, strong steric hindrance, direct conjugation of the substituent with the reaction centre) are well known.

The precision with which an empirical correlation equation can reproduce and/or predict the experimental quantities depends strongly on defining the range of validity. Too broad range includes many diverse cases deviating from the normal behaviour, with obvious consequences for the average accuracy. On the other hand, this accuracy cannot be enhanced as desired by simply restricting the range of validity since the differences between the individual experimental values will gradually diminish and finally fade out in the experimental error. The latter is supposed to be smaller than the mean difference between calculated and experimental values and hence it represents the utmost limit of the attainable precision of the correlation.

It has been intuitively felt and stated more or less explicitly¹ that there should be an optimum between the two above mentioned extremes, *i.e.* a medium range of validity with a good precision and sufficiently variable values. This postulate may be formulated more exactly when defining first the precision of the correlation by the root mean square difference (s) of predicted (x') and calculated (x) values:

$$s = \left[\sum_{i=1}^N (x'_i - x_i)^2 / (N - M) \right]^{1/2}. \quad (1)$$

Here N denotes the number of all data and M the number of adjustable parameters in the correlation equation. Similarly the extent of experimental values is characterized

by their standard deviation (s_0) from their average:

$$s_0 = \left[\sum_{i=1}^N (x_i - \bar{x})^2 / (N - 1) \right]^{1/2} . \quad (2)$$

The ratio $\psi = s/s_0$ was suggested² as a statistic characterizing the utility of the empirical relation;* for a valid relationship it ought to be less than 0.1 or 0.2 at worst.

The requirement of the optimum range of validity may be formulated:

$$s/s_0 = f(N) = \min . \quad (3)$$

This merely symbolic expression assumes N to be simply an independent variable, it means that there is a natural system of expanding continuously the validity range so that for a given N this range is unambiguously defined. Since this is clearly not possible in general, the best range is very difficult to find even when the optimum exists. For this reason, many well-known empirical relationships are to be viewed as not completely solved problems³.

In most LFE relationships the validity is restricted in two directions: as to the structure of the substrate and as to the type of reaction, or physical property *etc.* The Hammett equation, the classical prototype, is characterized³ by a severe restriction as to the structure (*meta* benzene and *para* derivatives without strong conjugation between the substituent and reaction centre), but almost no restriction as to the reaction (any reaction or physical quantity localized at the side-chain). Further development was oriented towards higher precision by eliminating even structures with weak conjugation; in this manner the so-called σ^0 -reactivity is defined⁴. The LFER's involving widely variable structures but restricted as to the type of reaction are very scarce^{5,6}.

In this note we search for the optimum range of validity of several selected correlations by an empirical approach; the main purpose was to prove on an experimental basis that such an optimum exists. In order to avoid any arbitrariness in choosing the empirical constants (σ), these were completely omitted and two direct experimental quantities were always correlated in a broad range of compounds.

RESULTS

Reaction Series

Three models were selected for which sufficient data were available:

* It is assumed that ψ has been determined on a large sample since its sampling distribution is not investigated². Under these conditions, ψ is a suitable statistic to evaluate the whole relationships, not the individual series or reactions. In the case of simple linear regression, ψ is (nonlinearly) related² to the correlation coefficient r .

1) Rate constants of the reaction of carboxylic acids with diphenyldiazomethane (ethanol, 30°C) against pK values of these acids in 80% methyl cellosolve.

2) The O—H stretching frequencies of carboxylic acids and phenols (in tetrachloromethane) against their pK values in water.

3) The pK values of primary ammonium ions $RNH_3^{(+)}$ against the pK values of the corresponding acids $RCOOH$ (both in water).

According to their structure the compounds were grouped into the following series with the increasing range of validity:

Series Hz (Hammett series, sigma zero reactivity): *meta* and *para* derivatives of phenylacetic acid and *meta* derivatives of benzoic acid. Relative values with respect to the unsubstituted acid are used.

Series Hr (Hammett series restricted to the standard compounds): *para* Derivatives of benzoic acid were added to the foregoing series; relative values.

Series H (classical Hammett series): *meta* and *para* Derivatives of aromatic and arylaliphatic acids; relative values with respect to the pertinent unsubstituted compound.*

Series Ho: The last series with the *ortho* derivatives added; relative values.

Series Th (Taft series⁷ restricted to hydrocarbon residues as substituents): Unsubstituted aliphatic, alicyclic, and arylaliphatic acids; absolute values.

Series Tr (Taft series⁷ as restricted by Charton⁸): Mono derivatives of acetic acid with various substituents; absolute values.

Series T (Taft series in the original conception⁷): Aliphatic, alicyclic and arylaliphatic acids with various substituents, sterically not overcrowded; absolute values.

Series N (sterically non-hindered compounds): Series H and T combined; absolute values.

Series A: All available data, absolute values.

In the model 2 carboxylic acids and phenols are correlated firstly separately, then together.

Choice of Data

The reliability of data was always of more weight than their great number. Hence the values were selected from critical compilations^{9,10} with respect to their indicated accuracy, or the whole sub-series was taken from one source whenever possible. Data from two sources were combined only when several overlapping entries allowed test of their agreement. Even so, in several cases, it appeared unavoidable to include some values denoted as less reliable or, with unknown precision.

The second order rate constants ($\text{mol}^{-1} \text{l min}^{-1}$) of the reaction of carboxylic acids with diphenyldiazomethane in ethanol at 30°C were not corrected for the parallel reaction with the solvent^{11,12}. They are available for benzoic acids with *meta*, *para* substituents^{11,13-15}, and *ortho* substituents¹², phenylacetic acids^{16,17}, cinnamic¹⁸ and α -phenylcinnamic¹⁹ acids *E* and *Z*, 8-substituted 1-naphthoic acids²⁰, 9-substituted 10-anthroic²⁰ and 10-triorthoic²⁰ acids, and various aliphatic and arylaliphatic acids²¹.

The apparent dissociation constants (in 80% methyl cellosolve by weight, at 25°C) of the above mentioned acids were taken mostly from Simon's collection²² with exception of cinnamic¹⁹, α -phenylcinnamic¹⁹, 1-naphthoic²⁰, 10-triorthoic²³ and several benzoic²⁴ acids.

* Quite rigorously the mere validity of the Hammett equation does imply the linear relationships in the series Hr but not in the series H. In the latter the condition of proportionality of ρ constants must be additionally fulfilled (the so-called¹⁶ ρ - q relation).

The thermodynamic dissociation constants of carboxylic acids in water at 25°C were taken mostly from the standard critical collection⁹ and completed by newer data for phenols²⁵. In the case of polysubstituted benzoic acids with *ortho* substituent (substituted toluic acids) the apparent dissociation constants in 1% ethanol²⁶ were substituted for the thermodynamic values; the error introduced is insignificant in a series with such striking deviations.

The O—H stretching frequencies in dilute tetrachloromethane solution relate in the case of carboxylic acids to the monomeric forms, and in the case of molecules with intramolecular hydrogen bonds always to the non-bonded forms. Data from several laboratories for *meta,para*-substituted²⁷, *ortho*-substituted²⁸ and polysubstituted^{26,28} benzoic acids were adjusted to the same calibration using the overlapping compounds. The two sources for phenols^{29,30} were roughly in agreement. The data for aliphatic acids^{28,31,32} could not be checked in this manner and were left unchanged.

The thermodynamic dissociation constants of primary ammonium ions in water at 25°C were taken completely from the critical compilation¹⁰.

Treatment of Data

The data were processed by a program for simple linear regression, choosing the first named quantity in each pair as the dependent variable and the second as the independent variable. This choice is of very little importance for the results. In order to eliminate possible experimental errors, the most deviating point of each series was automatically excluded and the regression repeated. According to the improvement achieved and with respect to the total number of points, the decision was made in each case by the operator, whether the pertinent point was to be rejected or not. Hence the final results for all the series do not depend sensitively on possible rejection of additional points. When a series was generated by mixing two different subseries (*e.g.* the series N from H and T), care was taken that these subseries contained comparable number of compounds. If necessary, the number of data was reduced by using the random sampling numbers.

The results of linear regressions are given in Table I; in addition to the statistics, the rejected data are also listed. Altogether they represent less than 4% of all the data.

For comparison, a simulated series was constructed as follows: The independent variable (x) was represented by randomly selected numbers with the normal distribution $N(0, 10)$. The dependent variable y_i was obtained as $y_i = x_i + \varepsilon_i$ where ε_i was another independent random variable with the distribution $N(0, 1)$. The results for several samples of different size are also given in Table I.

DISCUSSION

The main results are represented in Fig. 1. This shows the dependence of ψ (measuring the goodness of fit) on the number of compounds N . The dependence of the correlation coefficient r would yield the same picture after recalibrating the ordinate. The fundamental postulate is essentially confirmed, each curve showing a more or less pronounced minimum. The steep rise on the right-hand side is clearly due to exceeding the reasonable range of validity (the standard deviation s increases suddenly). The less distinct rise on the left-hand side is caused by an immoderate — sometimes quite arbitrary — restriction of the range of validity, resulting in reducing the variability of the data s_0 .

Before discussing the specific features of the optimum range of validity in each case, one must deal with two possible objections. Firstly the samples used may not be large enough to reach valid conclusions, particularly in the left-hand part of the graph. (Remember that ψ is defined for the infinite, or very large sample size.) Secondly the arranging of data into series according to structural features may be open to question; one may ask whether the system use is a reasonable one, or whether any reasonable system is possible at all.

As to the first problem concerning the sample size one must take into account that the pertinent populations are always finite, and when properly defined, they are even not too large. For instance the number of "all possible" Hammett substituents is strongly reduced in virtue of the following considerations³:

1) Too large substituents may violate the Hammett equation by their steric effects or a steric hindrance of solvation. 2) More complex substituents differing from each other only in their remote parts have virtually equal effects and may be counted as one substituent (*e.g.* COOR groups with variable R). 3) Very many structures are quite unstable or even unknown, and have

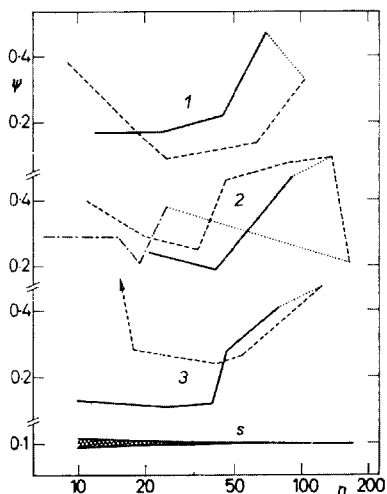


FIG. 1

The Accuracy of an Empirical Relationship ψ in Dependence on the Range of Validity (number of compounds N)

Reaction series 1–3 (Table I) and a randomly simulated series (S) are shown; full lines aromatic series, dashed lines aliphatic and mixed series, dot-and-dashed line phenols, dotted lines mixing of two series.

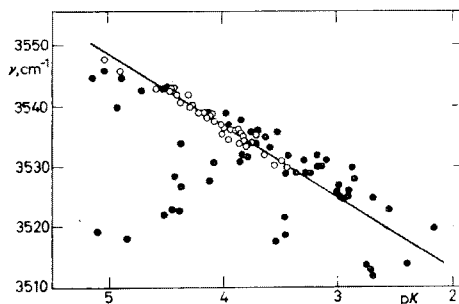


FIG. 2

Plot of the O—H Stretching Frequency *vs* pK 's of Substituted Benzoic Acids

○ *meta* and *para* derivatives, ● *ortho* derivatives.

TABLE I
Correlations of Two Experimental Quantities in Series of Compounds with Variable Range of Validity

Series	$ r ^a$	s^b	s_0^c	ψ^d	N^e	Slope ^f	Eliminated ^g
J) $\log k(\text{DDM})$ vs pK in 80% methyl cellosolve							
H _Z	0.9867	0.047	0.278	0.17	12	0.589	4-nitrophenylacetic acid
H _r	0.9864	0.054	0.319	0.17	24	0.510	—
H	0.9756	0.058	0.260	0.22	45	0.500	—
H _o	0.8876	0.130	0.281	0.47	71	0.542	—
Th	0.9342	0.094	0.246	0.38	9	0.650	—
Tr	0.9843	0.086	0.472	0.18	18	0.542	—
T	0.9955	0.077	0.788	0.09	26	0.538	—
N	0.9902	0.081	0.574	0.14	64	0.522	—
A	0.9458	0.180	0.552	0.33	104	0.545	—
2) $\nu(\text{OH})$ vs pK in water							
2a) Carboxylic acids							
H _Z	0.9733	0.64 ^h	2.71 ^h	0.24	21	-11.78 ^h	3-NH ₂ and 3-N(CH ₃) ₂
H _r	0.9813	0.80	4.12	0.19	42	-11.56	ditto + 4-OC ₆ H ₅ , 3-CH ₃ -4-NO ₂ and 3-CH ₃ -4-Br
H _o	0.8836	3.63	7.72	0.47	91	-10.65	ditto + 2-CH ₃ -6-NH ₂
Th	0.9259	1.31	3.31	0.40	11	-9.62	—
Tr	0.9601	1.51	5.26	0.29	20	-6.14	—
T ^j	0.9694	1.79	7.21	0.25	35	-5.77	triphenylacetic, atropic acids
T	0.8920	4.23	9.25	0.46	46	-6.95	ditto
N	0.8614	4.38	8.57	0.51	88	-7.64	ditto + 2-methyl-6-nitrobenzoic acid
A	0.8486	4.54	8.54	0.53	137	-8.13	—
2b) Phenols							
H _Z	0.9653	1.04	3.64	0.29	7	-6.71	3-OCH ₃ and 3-CHO
H _r ^k	0.9618	1.25	4.39	0.29	15	-6.71	ditto + 4-OH and 4-NH ₂
H _r	0.9786	1.24	5.87	0.21	19	-6.31	ditto
H _o	0.9271	2.26	5.91	0.38	25	-6.04	ditto

2c) Carboxylic acids and phenols together		6-46	30-12	0-21	167	— 12-69	—
A	0-9769						
3) pK's, amines vs carboxylic acids							
H _z ^l	0-9926	0-053	0-40	0-13	10	2-32	—
H _z	0-9946	0-109	1-03	0-11	25	3-04	4-nitrobenzylamine
H _l ^k	0-9926	0-122	0-99	0-12	40	2-92	ditto
H _r	0-9599	0-406	1-43	0-28	47	3-57	ditto
H _o	0-9120	0-912	2-25	0-41	81	2-48	ditto + 2-aminophenol and picramide
Th ^m	0-1506	0-065	0-063	1-04	11	0-17	—
Th	0-9625	0-156	0-56	0-28	18	2-32	—
Tr	0-9712	0-261	1-08	0-24	43	2-18	3-mercaptopropionic and 3,3,3-trifluoropropionic acids
T	0-9665	0-267	1-03	0-26	54	2-12	ditto + cyclopropanecarboxylic and t-2-methylcyclohexanecarboxylic acids
A	0-8840	1-871	3-99	0-47	123	3-87	as in H _o and T together
4) Simulated series							
—	0-9957	0-816	8-29	0-099	10	0-992	—
—	0-9969	0-690	8-24	0-084	10	1-021	—
—	0-9940	0-713	6-17	0-115	10	0-941	—
—	0-9962	0-936	10-18	0-092	10	1-022	—
—	0-9946	1-181	10-71	0-110	10	0-969	—
—	0-9961	0-733	8-05	0-091	20	1-005	—
—	0-9948	1-072	10-26	0-105	20	0-995	—
—	0-9958	0-748	7-99	0-094	30	0-998	—
—	0-9947	0-960	9-18	0-104	30	0-988	—
—	0-9957	0-794	8-48	0-094	40	1-007	—
—	0-9949	0-922	9-00	0-102	40	0-992	—
—	0-9952	0-872	8-87	0-098	50	0-997	—
—	0-9950	1	10-05	0-095	—	1	(expected values)

negligible chance of being included in any set. With this in mind we may estimate the number of different substituents to be not much more than 100 for each position. Hence the samples in Table I (series Hr) represent some 10% or even more of all possible data.

In other series the situation should not be very different. It is also true that the sampling is not random in this sense, that each possible compound has not an equal chance to be chosen, this chance being controlled mainly by preparative considerations. However, the sampling used is justified in the sense that more important and easily available compounds have a greater chance of being included. As to the absolute minimum number of compounds in a sample it seems that even 10 may be sufficient for the given purpose. From the simulated series (Fig. 1) with the purely random variance we may conclude that the much larger variation in other series are certainly not random; this applies even to sets with ten compounds only.

The problem of arranging data (*i.e.* compounds) into series is more delicate. The arrangement used in this paper (see Results) is based on the well-known correlation equations (Hammett, Taft), on their already tried extensions, and further on combinations of these series. Some justification of this procedure has been obtained *a posteriori* from the gradual loss of accuracy when extending the range of validity, and from the essential similarity between the models 1–3 (Table I, Fig. 1). Certainly, there are many other possible definitions of the range of validity and some of them could lead to new correlation equations; they could be revealed only by way of trial.

We conclude that the sample sizes are sufficient for the purpose intended, whereas the arrangement of the series seems to be acceptable but is not necessarily the best one. While any reasonable arrangement should allow to draw general qualitative conclusions, it cannot always disclose specific features of each series. With this in mind we can discuss some characteristic features of the series investigated.

In all the aromatic series, most striking is the loss of accuracy connected with including the *ortho* derivatives (Fig. 2). This is a well known phenomenon from the early development of the Hammett equation and is often quoted as a proof of the non-additive and non-proportional character of steric effects. Similar, but less pronounced, deviations are caused by the mesomeric effect of the substituent in the reaction series where direct conjugation with the reaction centre takes place (the so-called σ^- or σ^+ reactivity). In this paper it concerns series 3, see Fig. 3. In order to eliminate this conjugation completely, the σ^0 reactivity was defined^{4,33}. The results

Explanation to Table I

^a Absolute value of the correlation coefficient; ^b standard deviation from the regression line; ^c standard deviation of the dependent variable from its average value; ^d $\psi = s/s_0$; ^e number of points; ^f the slope corresponds to the ratio of the constants ρ for the two reactions; ^g the data which were eliminated from the sets, see Results; ^h the values of s , s_0 , and ρ are given in cm^{-1} within the whole section; ^j α, β -unsaturated acids excluded; ^k *para* acceptor substituents (σ_p^- reactivity) excluded; ^l only phenylacetic acids; ^m only alkanolic acids.

of this paper indicate that this restriction is not advantageous since a slight improvement of accuracy is more than outweighed by a too narrow range of validity, see all the series Hz in Table I. In the series H the validity of the $\rho - \rho$ relationship¹⁶

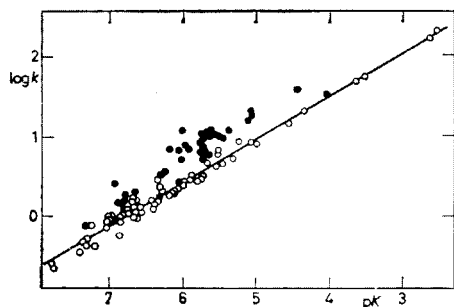


FIG. 3

Plot of pK 's, Aromatic Amines vs the Corresponding Benzoic Acids

○ *meta* Substituents and donor substituents in the *para* position, ● acceptor substituents in the *para* position.

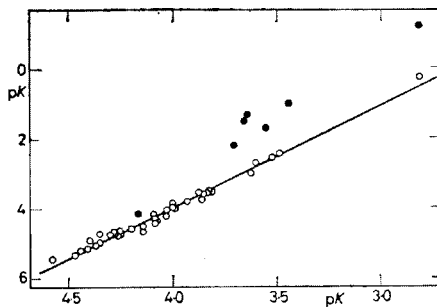


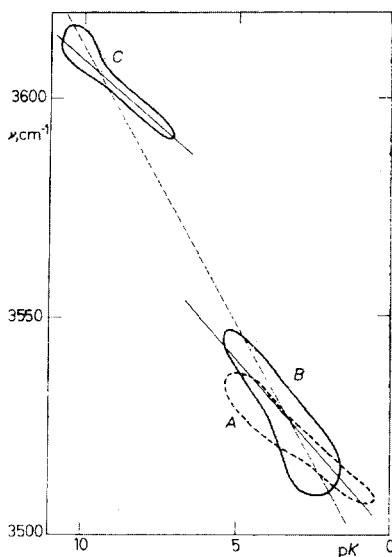
FIG. 4

Plot of the Rate Constants of the Reaction of Carboxylic Acids with DDM vs Their pK 's

○ Aliphatic sterically non-hindered and aromatic *meta* and *para* derivatives, ● aliphatic sterically hindered and aromatic *ortho* derivatives.

FIG. 5
Plot of the O—H Stretching Frequency vs pK 's of Various Acids

A aliphatic carboxylic acids, B aromatic and α,β -unsaturated acids, C phenols; full lines regression lines for carboxylic acids and phenols, respectively; broken line the apparent regression for the whole set.



(i.e. proportionally of ρ constants for various structures in the two reactions, e.g. pK and diphenyldiazomethane reaction) was assumed in addition to the Hammett equation. The accuracy was not significantly lowered; however, the experimental data were not quite sufficient for an effective test.

In the aliphatic series it is also the strong steric effect which causes the most striking deviations, see e.g. Fig. 4. It is, however, more difficult than in the aromatic series to define which derivatives are sterically hindered; in the case in Fig. 4 the decision was partly influenced by *ex post facto* arguments. The mesomeric effects cause deviations — similarly as in the aromatic series — only in certain reactions. In this paper it is the series 2, where α,β -unsaturated acids differ strongly from other aliphatic acids and rank with the aromatic ones (the lower part of Fig. 5). An extremely restricted range of validity is represented by the derivatives without heteroatoms (the series Th in Table I). These series are of no significance in practice; they were included here merely to demonstrate in a convincing manner the consequences of a too narrow range of validity. The small variability within the series is manifested in the values of s_0 in all these series.

We shall further mention the consequences of combining two sets which are actually different in nature, e.g. combining of aliphatic and aromatic derivatives together, as indicated in Fig. 1 by dotted lines. This combination usually results in a markedly lowered accuracy, see e.g. the series 1A, 2aA, 3A in Table I. An opposite result is encountered in the series 2cA: When carboxylic acids and phenols are mixed to give an artificial series, an apparent correlation with a fairly high correlation coefficient emerges. However, the pertinent graph (Fig. 5) consists of two independent and rather distant groups of points each of which has its own correlation line. The overall correlation line connects approximately the centres of gravity of the two sets and the correlation does not express anything more than that the two groups differ fundamentally from each other. Such a false correlation may be disclosed most easily by comparing the slopes of the correlation lines for the total set and the two sub-sets.

It follows that the classical Hammett and Taft equations with their original range of validity are more advantageous than all the modifications examined in this paper. The last result of the present analysis could be to disclose new possible ranges of validity which could form the basis for further correlation equations. The only promising possibility is in our opinion represented by a combination of aliphatic and aromatic sterically non-hindered derivatives (series N, see Fig. 4 empty points). The extended range of validity as to the substrate, compared with the Taft or Hammett equation, should be compensated by restrictions as to the types of reaction, e.g. to reactions of carboxylic acids. These possibilities should be explored on a broader experimental basis.

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