THE APPLICATION OF THE ACIDITY FUNCTION CONCEPT TO STRONGLY BASIC MEDIA

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1. Introduction

In dilute solutions of acids or bases the pH scale, which aims to equate acidity with hydrogen ion activity, is a useful concept. In concentrated solutions however the acidity (in the case of acids) or the reciprocal acidity (in the case of bases) increases much more rapidly than the stoicheiometric concentration of acid or base. In 1932 Hammett and Deyrup suggested that the acidity of concentrated solutions of strong acids might conveniently be equated with the ability of the acid solution to protonate a neutral solute (indicator) species.[1] This suggestion led to the Hammett acidity function. Other acidity functions have since been recognised: the subject was reviewed in 1957.[2] However most of the work then reviewed related to acid solution. There had been only four relevant studies of base solution before that. Since 1957 many further advances in the study and understanding of acid solutions have been made and there has also been an increasing number of results for concentrated base solutions. These results are reviewed here on the assumption that the reader is not familiar with the acidity function concept. As a directive to the literature a few references for acid solutions are given, particularly where parallel theories for strongly acidic and strongly basic media exist. Recent measurements have shown that Hammett's early ideas require modification for concentrated acid solutions since the Hammett acidity function is not unique but differs for different classes of indicator. Acidity functions for base solutions are also apparently dependent on indicator structure. Despite this the general theme is here developed following the postulates of Hammett and modifications to the basic ideas are introduced where experimental results are presented which suggest their necessity.

2. The H_- Acidity Function in Aqueous Alkali-metal Hydroxide Solutions

(*a*) **Definition and Measurement of the H_- Function.**—The H_- acidity function for a given base solution is a measure of the ability of that solution to abstract a proton from an electrically neutral weakly acidic indicator molecule SH according to the ionisation equilibrium (1).[2]

$$\mathrm{SH} + \mathrm{OH}^- \rightleftharpoons \mathrm{S}^- + \mathrm{H_2O} \qquad (1)$$

The numerical value of H_- is defined by eqn. (2), where a represents an activity, f an activity coefficient (such that $a_{\mathrm{SH}}=f_{\mathrm{SH}}[\mathrm{SH}]$), and

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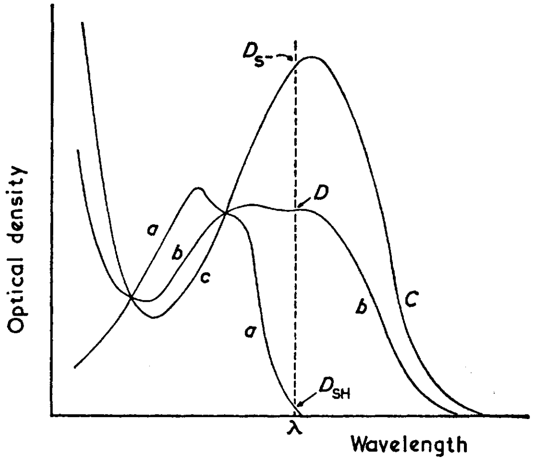
[1] L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.
[2] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, (*a*) 1, (*b*) 935.

$K_{SH}=a_{H^+}a_{S^-}/a_{SH}$ is the acid ionisation constant of SH.

$$H_-= -\log_{10}(a_{H^+}f_{S^-}/f_{SH})=pK_{SH} + \log_{10}([S]^-/[SH]) \qquad (2)$$

To establish the H_- scale for a series of base solutions of increasing hydroxide-ion concentration, measurement of pK_{SH} and the variation of $\log_{10}([S^-]/[SH])$ with hydroxide ion concentration is necessary. The most convenient method for this is ultraviolet or visible spectrophotometry with the proviso that S^- and SH must have measurably different electronic absorption spectra. The Figure shows a typical series of spectra of the same stoicheiometric concentration ($[SH]_{stoich}$, usually *ca.* 10^{-4}M) of an acid indicator in solutions containing three different concentrations of an alkali-metal hydroxide MOH in water. It is important to have established that the changes in spectra for a particular indicator SH are relevant to equilibrium (1) and not to a base-addition reaction or an equilibrium involving interaction of SH with more than one hydroxide ion. Simple diagnosis of modes of ionisation in aqueous hydroxide and alcoholic alkoxide solutions has proved difficult although n.m.r. spectroscopy is sometimes informative.[3] Spectrum (*a*) refers to an MOH concentration in which equilibrium (1) is practically entirely on the left and is therefore the spectrum of un-ionised SH. Conversely solution of SH in a high concentration of MOH enables the spectrum (*c*) of S^- to be determined. Spectrum (*b*) is for an intermediate concentration of MOH in which an appreciable amount of SH and S^- exist. At the wavelength λ the extinction coefficients ϵ of SH and S^- are given by $D_{SH}=\epsilon_{SH}[SH]_{stoich}$ and $D_{S^-}=\epsilon_{S^-}[SH]_{stoich}$.



Typical electronic absorption spectra of a weak acid (at a fixed stoicheiometric concentration) in three solutions of different base strengths. Details are given in the text.

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[3] M. R. Crampton and V. Gold, *Proc. Chem. Soc.*, 1964, 298; W. P. Norris and J. Osmundsen, *J. Org. Chem.*, 1965, **30**, 2407.

Assuming that the Beer–Lambert Law[4] holds for SH and S^- in the solutions under investigation the optical density D at λ in spectrum (*b*) will be given by $D=\epsilon_{SH}[SH]+\epsilon_{S^-}[S^-]$ where [SH] and $[S^-]$ represent the concentrations of SH and S^- in equilibrium in the particular MOH solution. Combination of this equation with the material balance $[SH]+[S^-]=[SH]_{stoich}$ leads to eqn. (3) from which $([S^-]/[SH])$ is calculable. The

$$([S^-]/[SH])=(D-D_{SH})/(D_{S^-}-D) \qquad (3)$$

result should be independent of the wavelength. Measurement of a series of spectra enables the variation of $([S^-]/[SH])$ with MOH concentration to be established. In general a particular indicator only gives reliable results for the small range of MOH concentrations in which $(D-D_{SH})$ and $(D_{S^-}-D)$ are accurately measurable. For information over a wide range of MOH concentrations a series of indicators of different acidity would have to be studied.

Evaluation of pK_{SH} may be made from the spectrophotometric results by one of two methods. For the more acidic indicators use is made of eqn. (4) in which a_w is the activity and K_w is the ionic product of the

$$pK_w-pK_{SH}=\log_{10}([S^-]/[SH])-\log_{10}[OH^-]+\log_{10}(f_{S^-}a_w/f_{SH}f_{OH}) \qquad (4)$$

solvent water. At infinite dilution a_w and all activity coefficients are by definition unity and therefore extrapolation of a graph of $\log_{10}([S^-]/[SH])-\log_{10}[MOH]$ against [MOH] to $[MOH]=0$ gives a value for (pK_w-pK_{SH}) and hence for pK_{SH}.[5] These plots are usually nearly linear and the extrapolation is therefore reliable. For more weakly acidic indicators the extrapolation is unreliable and a stepwise procedure is adopted. This method requires the basic postulate that for a series of indicators both $d\log_{10}([S^-]/[SH])/d[MOH]$ and H_- for a particular MOH concentration are independent of indicator. It follows from this and eqn. (2) that if the ranges of MOH concentrations which can be studied by two different indicators SH and RH overlap, then in the region of overlap

$$pK_{SH}+\log_{10}([S^-]/[SH])=pK_{RH}+\log_{10}([R^-]/[RH]) \qquad (5)$$

Suppose now that for SH, the stronger acid, the above described extrapolation method is reliable and pK_{SH} has been determined. Then pK_{RH} can be evaluated from eqn. (5). Choice of a series of progressively weaker indicators such that successive acids ionise in overlapping regions of MOH concentration allow the acid ionisation constants of all the indicators to be deduced. Subsequent substitution in eqn. (2) of pK_{SH} and values of $([S^-]/[SH])$ for each indicator then defines the H_- acidity function. In

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[4] J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules," Methuen, London, 1963.

[5] R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5030.

general the experimental method for the determination of any other acidity function in either acidic or basic media is analogous to the above.[2a]

(*b*) Experimental H_- Scales for Aqueous Alkali-metal Hydroxides.—Only four sets of measurements of H_- acidity functions for aqueous alkali-metal hydroxides have been made.[6–9] This paucity of data can be attributed to the salting-out of many suitable indicators in strong aqueous electrolyte, the possibility of reversible hydroxide addition to, rather than proton abstraction from, the indicator, and the tendency for irreversible substitution reactions to occur.

On the assumption that $H_-=14$ when [MOH]=1M, Schwarzenbach and Sulzberger have quoted for aqueous NaOH and KOH H_- scales (Table 1) measured by use of indigo derivatives as indicators.[6] These were added to the aqueous alkali in an immiscible solvent, the mixture of two phases being allowed to reach equilibrium before colorimetric analysis. Providing the partition coefficients of the neutral indicators between the two layers are independent of the concentration of alkali in the aqueous phase this technique is reliable. Edward and Wang have shown that the ionisation of thioacetamide in aqueous NaOH parallels the data of Schwarzenbach and Sulzberger up to [NaOH]=5M.[7]

TABLE 1. *Experimental* H_ *acidity function scales for aqueous alkali-metal hydroxides.*

[MOH] (M)	$pK_W + \log_{10}[MOH]^a$ (20°)	$H_-(KOH)^b$ (20°)	$H_-(NaOH)^b$ (20°)	$H_-(LiOH)^c$ (25°)
1	14·17	14·00	14·00	13·43
2	14·47	14·49	14·36	13·53
3	14·65	14·81	14·64	13·93
4	14·77	15·12	14·93	14·04
5	14·87	15·45	15·14	14·31
6	14·95	15·74	15·37	
8	15·07	16·39	15·76	
10	15·17	17·22	16·17	
12	15·25	18·12	16·72	
14	15·32		17·37	
16	15·37		18·13	
18	15·43		18·68	

[a] $pK_W(20°) = 14·17$; H. S. Harned and R. A. Robinson, *Trans. Faraday Soc.*, 1949, **36,** 973. [b] G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, 1944, **27,** 348. [c] R. Stewart and J. P. O'Donnell, *Canad, J. Chem.*, 1964, **42,** 1681.

Equation (6) follows from eqn. (2). For NaOH and KOH up to 1M the

$$H_-=pK_W + \log_{10}[OH^-] + \log_{10}(f_{SH}f_{OH^-}/f_{S^-}a_W) \qquad (6)$$

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[6] G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, 1944, **27,** 348.
[7] J. T. Edward and I. C. Wang, *Canad, J. Chem.*, 1962, **40,** 399.
[8] R. Stewart and J. P. O'Donnell, *Canad. J. Chem.*, 1964, **42,** 1681.
[9] V. I. Lazarev and Yu. V. Moiseev, *Zhur, fiz. Khim.*, 1965, **39,** 445.

last term of eqn. (6) approximates to zero and H_- corresponds to the "ideal" expression ($pK_W + \log_{10}[OH^-]$).[7] Comparison of H_- with ($pK_W + \log_{10}[MOH]$) for $[MOH] > 1$M shows a deviation between the experimental H_- scales and "ideality" which increases rapidly with increasing base concentration (Table 1). Substitution of known water activities in eqn. (6) only partially accounts for the deviation. Unfortunately nothing is known about the variation with alkali concentration of the solute activity coefficients f_{SH} and f_{S^-}.

An H_- scale (Table 1) for aqueous lithium hydroxide solutions up to 5M has also been measured.[8]

(*c*) **Theoretical Predictions of H_- on the Solvation Model.**—Attempts have been made to calculate H_- values theoretically by use of parallel methods to that developed by Bell and Bascombe[10] for calculation of the Hammett acidity function for strong mineral acids. The ionisation of a weak acid in aqueous hydroxide is considered to be correctly written as

$$SH + OH^- \rightleftharpoons S^- + (n + 1)H_2O \qquad (7)$$

where n has been taken either as the hydration number of the OH^- ion[11] or as the difference in hydration numbers between ($SH + OH^-$) and S^-.[7] In either case eqn. (6) becomes

$$H_- = pK_W + \log_{10}[OH^-] - (n + 1)\log_{10}a_W + \log_{10}(f_{SH}f_{OH^-}/f_{S^-}) \qquad (8)$$

This equation cannot be rigorously tested because although water activities are known there are no results for the activity coefficient term. Edward and Wang, however, assuming that $\log_{10}(f_{SH}f_{OH^-}/f_{S^-}) \sim x \log_{10} a_W$, have shown, taking $[OH^-]=[NaOH]$ and $(n + 1 - x)=3{\cdot}2$, that for aqueous NaOH < 5M good agreement between the experimental and theoretical H_- scales is obtained.[7]

Yagil and Anbar considered a slightly different approach in which $\log_{10}(f_{SH}f_{OH^-}/f_{S^-})$ was equated to zero, n ($=3$) was taken as the hydration number of the OH^- ion, and in place of a_W was substituted the concentration of free water (*i.e.*, that water which is not bound to OH^- in solvation).[11] Good agreement with experiment for $[NaOH] < 8$M was obtained. However for aqueous KOH the results were less satisfactory. Two sets of parallel calculations using mole fractions and volume fractions instead of molar concentrations of hydroxide ion and free water were also made and gave similar results, although whereas for aqueous NaOH the molar concentration scale gave the best agreement with experiment, for KOH the volume fraction scale was best.

It may be concluded that the simple Bell and Bascombe treatment is applicable to moderately concentrated (up to *ca.* 5M) alkali solutions although it breaks down in more concentrated solutions. This is not sur-

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[10] R. P. Bell and K. N. Bascombe, *Discuss. Faraday Soc.*, 1957, **24**, 158.
[11] G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, 1963, **85**, 2376.

prising in view of the sweeping assumptions which have to be made regarding the activity coefficient term in eqn. (8). Also it is almost certain that the factor n in the above equations is not constant but decreases with increasing base concentration.[12] The assumption that $[OH^-]=[MOH]$ is also suspect owing to the possibility of ion association, the extent of which for a particular molar concentration of metal hydroxide is in the order LiOH > NaOH > KOH.[13] Providing it is assumed that the associated species contribute less than hydroxide ions to H_- this would be consistent with the observed order of basicity H_-(LiOH) < H_-(NaOH) < H_-(KOH).

(*d*) **Correlation of Reaction Rates with the H_- Function.**—The correlation of the H_- function with rate constant has been studied for several base-catalysed reactions.[14,15] Consider a reaction (*e.g.*, the alkaline hydrolysis of chloroform) of mechanism (9)

$$\begin{array}{ll} SH + OH^- \rightleftharpoons S^- + H_2O & S^- \rightarrow \text{products} \\ \text{rapid pre-equilibrium} & \text{rate-determining } (k') \\ \quad [S^-] \ll [SH] & \end{array} \qquad (9)$$

for which the experimental rate constant k_{obs} is given by

$$k_{obs} = -(1/[SH])(d[SH]/dt) = k'([S^-]/[SH])(f_{S^-}/f^*) \qquad (10)$$

If, by analogy with the Zucker–Hammett hypothesis for acid solution,[2b,16] the equality $(f_{SH}/f^*)=(f_{SH}/f_{S^-})$ is assumed then combination of eqns. (2) and 10 leads to

$$\log_{10}k_{obs} = \log_{10}(k'K_{SH}) + H_- \qquad (11)$$

Hence $\log_{10}k_{obs}$ should be a linear function of H_- with unit slope.

An alternative approach follows from combination of eqns. (11) and (8) [with the assumption $\log_{10}(f_{SH}f_{OH^-}/f_{S^-}) \sim 0$]:[15]

$$\log_{10}(k_{obs}/[OH^-]) = \log_{10}(k'K_{SH}/K_w) - (n+1)\log_{10}a_w \qquad (12)$$

If eqn. (12) is valid a plot of $\log_{10}(k_{obs}/[OH^-])$ against $\log_{10}a_w$ gives a value for n which could be looked upon as the change in number of solvated water molecules in passing from reactants to the transition state in the rate-determining step. This is an extreme interpretation. By analogy with Bunnett's observations[17] for acid solution it is probable that n is a function of both the mechanism of the reaction and the chemical structure of the reacting solute SH. Experimental results for methanolic sodium methoxide solutions confirm this point (Section 4*b*). Yagil and Anbar consider that the use of the free water concentration rather than the water

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[12] G. F. Freeguard, R. B. Moodie, and D. J. G. Smith, *J. Appl. Chem.*, 1965, **15**, 179.

[13] L. S. Darken and H. F. Meier, *J. Amer. Chem. Soc.*, 1942, **64**, 621.

[14] G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, 1962, **84**, 1797.

[15] M. Anbar, M. Bobtelsky, D. Samuel, B. Silver, and G. Yagil, *J. Amer. Chem. Soc.*, 1963, **85**, 2380.

[16] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

[17] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.

activity provides a better indication of the number of water molecules involved in the formation of the transition state.[15]

It must be noted that for eqn. (11) to apply the factor n for the reaction being studied must be the same as that for eqn. (7) applied to the particular acid indicators used to measure the H_- scale with which the rate constants are being correlated. If this condition is not satisfied the plot of $\log_{10}k_{\mathrm{obs}}$ against H_- will not have unit slope.

Reactions for which rates have been correlated with H_- include the base-catalysed formation of hydrazine from chloramine and ammonia,[14] and the elimination reaction of DL-serine phosphate to form pyruvate, phosphate, and ammonia.[15] H_- Scales for aqueous lithium hydroxide and cæsium hydroxide have been suggested from the rates of hydrolysis of carbon disulphide in these media.[9] The H_- values were interpolated from the plot of H_- against rate constant for aqueous sodium and potassium hydroxides.[18] The scale for lithium hydroxide is in accord with equilibrium measurements.[8]

3. The J_- Acidity Function

(*a*) **Hydroxide Addition. The Definition of J₋.**—The J_- acidity function describes the ability of an aqueous base solution to add hydroxide ions to a neutral indicator molecule R.[19] Thus eqn. (13) defines J_- where K is the association constant for the

$$J_-=\log_{10}(a_{\mathrm{H^+}}f_{\mathrm{ROH^-}}/f_{\mathrm{R}}a_{\mathrm{w}})=\mathrm{p}(KK_{\mathrm{w}})+\log_{10}([\mathrm{ROH^-}]/[\mathrm{R}]) \qquad (13)$$

formation of the addition complex ROH⁻. By analogy with eqn. (7) it is probable that the association equilibrium is best written as

$$\mathrm{R}+\mathrm{OH^-}\rightleftharpoons\mathrm{ROH^-}+m\mathrm{H_2O} \qquad (14)$$

This leads to eqn. (15) for J_- and eqn. (16) for the relationship between

$$J_-=\mathrm{p}K_{\mathrm{w}}+\log_{10}[\mathrm{OH^-}]-m\log_{10}a_{\mathrm{w}}+\log_{10}(f_{\mathrm{OH^-}}f_{\mathrm{R}}/f_{\mathrm{ROH^-}}) \qquad (15)$$

H_- and J_- (cf. that between H_0 and J_0 in acid solution[2a]). Ideally, paralleling of indicator equilibria in aqueous alkali solution with H_- or

$$J_-=H_-+(n-m+1)\log_{10}a_{\mathrm{w}}+\log_{10}(f_{\mathrm{R}}f_{\mathrm{S^-}}/f_{\mathrm{ROH^-}}f_{\mathrm{SH}}) \qquad (16)$$

J_- should enable proton–abstraction and hydroxide-addition reactions to be differentiated. Unfortunately no J_- scale has yet been measured for aqueous alkaline solutions although several rate studies involving hydroxide addition to a neutral substrate have been made.[15,20,21]

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[18] V. I. Lazarev and Yu. V. Moiseev, *Zhur. fiz. Khim.*, 1965, **39**, 376.

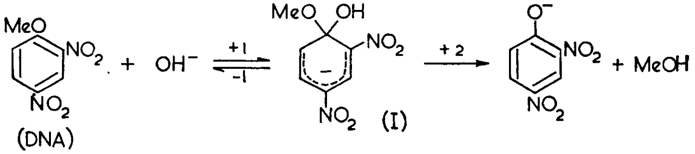
[19] V. Gold and B. W. V. Hawes, *J. Chem. Soc.*, 1951, 2102; V. Gold and C. H. Rochester, *ibid.*, 1964, 1722; C. H. Rochester, *Trans. Faraday Soc.*, 1963, **59**, 2820.

[20] C. H. Rochester, *Trans. Faraday Soc.*, 1963, **59**, 2826.

[21] G. Yagil and M. Anbar, *J. Amer. Chem. Soc.*, 1962, **84**, 1790.

(*b*) **Correlation of Reaction Rates with J₋.**—The observed rate constant k_{obs} for a bimolecular nucleophilic substitution involving attack by the hydroxide ion on the reacting substrate should parallel the J_- acidity function. Such a reaction is the alkaline hydrolysis of 2,4-dinitroanisole[20] for which the reactions shown in Scheme 1 are probable.

SCHEME I



(17)

In accord with the observation that a negligible concentration of the intermediate complex (I) is present in the reaction solution it follows that

$$k_{\text{obs}} = -(1/[\text{DNA}])(\text{d}[\text{DNA}]/\text{d}t) = k_2K_1[\text{OH}^-](f_{\text{DNA}}f_{\text{OH}^-}/f^*) \quad (18)$$

whence by analogy with the assumptions made in section 2*d*

$$\log_{10}k_{\text{obs}} = \log_{10}(k_2K_1K_{\text{W}}) + J_- \quad (19)$$

To test this equation and in the absence of measurements of the J_- function the approximation

$$J_- = H_- + \log_{10}a_{\text{W}} \quad (20)$$

has to be used. This follows from eqn. (16) with the assumptions that $\log_{10}(f_{\text{R}}f_{\text{S}^-}/f_{\text{SH}}f_{\text{ROH}^-}) \sim 0$ and that n (for the indicators used by Schwarzenbach and Sulzberger) equals m (for dinitroanisole). Although these assumptions are somewhat questionable a plot of $\log_{10}k_{\text{obs}}$ against $(H_- + \log_{10}a_{\text{W}})$ for the hydrolysis in aqueous sodium hydroxide gave a good linear plot with slope 1·1 over a seventy-fold range of reaction rate.[20] Slopes of unity were also obtained in similar studies of the hydrolyses of ethyl iodide[15] (in aqueous KOH) and of dimethylchloramine[21] (in aqueous KOH and aqueous NaOH), both $S_{\text{N}}2$ reactions, although here the concentrations of free water rather than the water activities were substituted in eqn. (20).

The mechanistic significance of the H_- and J_- functions can be seen from the following example. Two possible mechanisms have been suggested for the hydrolysis of chloramine in aqueous alkali namely, a pre-equilibrium involving proton transfer from chloramine to give the ion NHCl^- which reacts with solvent water to give hydroxylamine, or a nucleophilic attack of hydroxide ions on the chloramine substrate.[21] Yagil and Anbar strengthened their supposition that the latter was correct by showing that $\log_{10}k_{\text{obs}}$ plotted against H_- gave a slope of 0·92 whereas plotted against

$H_- + \log_{10}[H_2O]_{free}$ a slope of exactly unity resulted. In considering the validity of this result however the sweeping assumptions made in the acidity function treatment must not be lost sight of.

4. Acidity Functions for Solutions of Alkali-metal Methoxides in Methanol

(*a*) **The H_M[†] Acidity Function.**—The H_M acidity function is pertinent to the ionisation of a weakly acidic neutral solute molecule AH in methanol solution according to

$$AH + OMe^- \rightleftharpoons A^- + (p + 1)MeOH \qquad (21)$$

where the factor p has a similar significance to n in equilibrium (7). By analogy with the corresponding equations for H_- in aqueous solution:

$$H_M = -\log_{10}(a_{H^+} f_{A^-}/f_{AH}) = pK_{AH} + \log_{10}([A^-]/[AH]) \qquad (22)$$

$$= pK_{MeOH} + \log_{10}[OMe^-] - (p + 1)\log_{10} a_{MeOH} + \log_{10}(f_{AH} f_{OMe^-}/f_{A^-}) \qquad (23)$$

where K_{MeOH} is the ionic product (16·7 at 25°)[22] and a_{MeOH} is the activity of the solvent methanol.

The H_M function for methanolic sodium methoxide solutions has been measured by use of substituted anilines and diphenylamines,[5,23] or phenols[24,25] as indicators following the experimental method described in section 2. The results are given in Table 2 and show that the H_M function is not unique but varies with the particular indicator used to measure it. This is in accord with observed deviations between the ionisation behaviour of weak bases of different structure in concentrated acid solutions.[26]

Inspection of eqn. (23) leads to the conclusion that the deviations in H_M may be due to variation with indicator structure of either $\log_{10}(f_{HA}/f_{A^-})$ or p. Here, as in acid solution, the latter has been preferred although it is to some extent a case of shunning discussions on activity coefficients on account of ignorance of their behaviour. However comparison of the three H_M functions defined by the ionisation of phenols is apparently informative on this point.

[†] Several workers recommend the use of subscript M to denote acidity functions which refer to methanol as the standard state. This nomenclature is used here so there is a clear distinction from the corresponding functions for water as standard state.

[22] R. P. Bell, "The Proton in Chemistry," Methuen, London, 1959, ch. 4.

[23] R. Schaal and G. Lambert, *J. Chim. phys.*, 1962, 1164.

[24] C. H. Rochester, *J. Chem. Soc.*, 1965, 676.

[25] C. H. Rochester, *J. Chem. Soc.* (*B*), 1966, 121.

[26] A. J. Kresge, G. W. Barry, K. R. Charles, and Y. Chiang, *J. Amer. Chem Soc.*, 1962, **84,** 4343; J. T. Edward and I. C. Wang, *Canad. J. Chem.*, 1962, **40,** 966; A. R. Katritzky, A. J. Waring, and K. Yates, *Tetrahedron*, 1963, **19,** 465; K. Yates, J. B. Stevens, and A. R. Katritzky, *Canad. J. Chem.*, 1964, **42,** 1957; R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, 1964, **86,** 3796; F. A. Long and J. Schulze, *ibid.*, 1964, **86,** 327.

TABLE 2. *Experimental acidity function scales for methanolic sodium methoxide*

[NaOMe] (M)	$H_M(25°)^a$	$H_M(25°)^b$	$H_M(25°)^c$	$H_M(20 \pm 3°)^d$	$J_M(25°)^e$
0·1	15·75	15·75	15·75		
0·25	16·17	16·14	16·18	16·26	
0·5	16·50	16·51	16·53	16·66	
1·0	16·89	16·91	16·97	17·23	
1·5	17·15	17·22	17·33	17·71	18·32
2·0	17·38	17·56	17·70	18·10	19·01
2·5	17·60	17·93	18·07	18·52	19·75
3·0			18·51	18·98	20·44
3·5				19·53	21·15
4·0				20·20	

Indications were as follows:
[a] Pentamethylphenol: C. H. Rochester, *J. Chem. Soc.* (*B*), 1966, 121. [b] *o*-t-Butylphenols: C. H. Rochester, *J. Chem. Soc.*, 1965, 676. [c] 2,6-Di-t-butylphenols: C. H. Rochester, *J. Chem. Soc.*, 1965, 676. [d] Nitrogen acids: R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5030. [e] 2,4-Dinitroanisole: C. H. Rochester, *J. Chem. Soc.*, 1965, 2404.

Infrared[27] and n.m.r.[28] evidence suggests that the order 2,6-dimethyl < *o*-t-butyl < 2,6-di-t-butyl represents the relative abilities of these substituents in a phenol to hinder the approach of a second molecule to the oxygen atom of the phenol group. The values of the acid ionisation constants[24] of the substituted phenols lead to the assumption that these effects are also reflected in the solvation numbers of the corresponding phenoxide anions.[25,29] This would suggest that p(2,6-diMe) < p(*o*-Bu^t) < p(2,6-di-Bu^t) which is in accord with the observed deviations of the three phenol H_M functions from each other.

Attempts to estimate numerical values for p by a Bell and Bascombe type treatment have met with little success,[12,24] probably because the assumption $\log_{10}(f_{AH}f_{OMe^-}/f_{A^-}) \sim 0$ is not valid in methanol.

H_M scales for methanolic potassium and lithium methoxide solutions have been measured by use of substituted anilines and diphenylamines as indicators.[23,30] For a particular stoicheiometric molarity of base H_M(LiOMe) < H_M(NaOMe) < H_M(KOMe). Reasons for this order have not been discussed although the effect of ion association on acidity is perhaps of some importance.

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[27] N. D. Coggeshall, *J. Amer. Chem. Soc.*, 1947, **69**, 1620; W. C. Sears and L. J. Kitchen, *ibid.*, 1949, **71**, 4110; L. Hunter, *Progr. Stereochem.*, 1954, **1**, 223; L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc.*, 1960, *A*, **254**, 119; L. J. Bellamy, G. Eglington, and J. F. Morman, *J. Chem. Soc.*, 1961, 4762; K. U. Ingold and D. R. Taylor, *Canad. J. Chem.*, 1961, **39**, 481.

[28] V. F. Bystrov and V. P. Lezina, *Optics and Spectroscopy*, 1964, **16**, 542; B. G. Somers and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1963, **85**, 3065.

[29] C. H. Rochester, *J. Chem. Soc.*, 1965, 4603.

[30] R. Schaal and F. Peuré, *Bull. Soc. chim. France*, 1963, 2636; F. Terrier and R. Schaal, *Compt. rend.*, 1965, **260**, 5567; R. Schaal and G. Lambert, *ibid.*, 1962, 2256.

(*b*) **Correlation of Reaction Rates with H_M.**—More O'Ferrall and Ridd have studied the variation of reaction rate with sodium methoxide concentration for the methanolyses of chloroform, phenethyl chloride, and 1-chloro-3,3-dimethylbutane.[31] The established mechanisms of these reactions can be contracted to

$$\underset{\text{fast}}{CHCl_3 + OMe^- \rightleftharpoons CCl^-_3 + MeOH} \qquad \underset{\text{slow}}{CCl^-_3 \rightarrow \text{products}} \qquad (24)$$

for chloroform (classified as *B*1), and

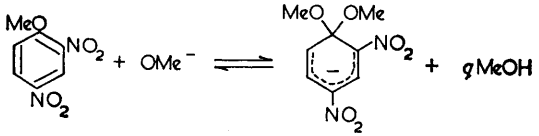
$$\underset{\text{slow (bimolecular)}}{SH + OMe^- \rightarrow \text{products}} \qquad (25)$$

for phenethyl chloride (*E*2 elimination) and 1-chloro-3,3-dimethylbutane (concurrent *E*2 elimination and S_N2 substitution).

The first-order rate constants ($k' = -\,d\ln[SH]/dt$) for 1-chloro-3, 3-dimethylbutane were proportional to sodium methoxide concentration whereas for phenethyl chloride the dependence ranged from first order in dilute solution to about third order in [NaOMe]=4M. For chloroform the increase in apparent order in methoxide was greater, and a plot of $\log_{10}k_1$ against H_M gave a curve with an average slope of 0·8 in the range 1M < [NaOMe] < 3M.

These results can be rationalised by considering that the difference in solvation between the reactants and the transition state is not the same for the three reactions. Increasing the sodium methoxide concentration lowers the solvent activity and this will have the greatest effect on the rates of reactions for which the difference in solvation is large. This conclusion is deemed logical in the present instance since, if loss of solvation of the methoxide ion is the most important factor, comparison of reactions (24) and (25) show that for the *B*1 mechanism the methoxide ion is completely neutralised before the transition state is reached, whereas for the *E*2 elimination only partial neutralisation has occurred. It is apparent from the above that many more such studies are necessary before correlation of reaction rates with the H_M function (or with base concentration) can be expected to give unambiguous mechanistic information about previously unstudied reactions.

(*c*) **The J_M Acidity Function. Methoxide addition.**—A J_M acidity function (Table 2) has been measured[32] by use of 2,4-dinitroanisole as indicator, which with methoxide ions forms an addition complex of 1:1 stoicheiometry according to reaction (26).



(26)

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[31] R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5035.
[32] C. H. Rochester, *J. Chem. Soc.*, 1965, 2404.

By analogy with J_- (eqn. 15) it follows that (B being written for dinitroanisole and BOMe⁻ for the addition complex):

$$J_M = pK_{MeOH} + \log_{10}[OMe^-] - q \log_{10} a_{MeOH} + \log_{10}(f_{OMe^-} f_B / f_{BOMe^-}) \qquad (27)$$

which combined with eqn. (23) leads to

$$J_M = H_M + (p + 1 - q)\log_{10} a_{MeOH} + \log_{10}(f_B f_{A^-} / f_{BOMe^-} f_{AH}) \qquad (28)$$

The J_M scale deviates about twice as much from $pK_{MeOH} + \log_{10}[OMe^-]$ as the H_M scales although whether this is due to $q > (p + 1)$ or a large deviation of $(f_B f_{A^-} / f_{BOMe^-} f_{AH})$ from unity is a matter of conjecture.

The rates of the S_N2 reactions of *o*- and *p*-dinitrobenzene with methoxide ions to form *o*- and *p*-nitroanisole respectively have been measured by Schaal, Latour, and Peuré with methanolic LiOMe, NaOMe, and KOMe as sources of methoxide ions.[33] Following similar arguments to those which led to eqns. (19) and (20) for aqueous solution, correlation of $\log_{10} k_{obs}$ with $(H_M + \log_{10}[MeOH])$ gave a series of plots with unit slope. The H_M functions were measured with anilines and diphenylamines as indicators,[23,30] and [MeOH] was taken as the concentration of free methanol, calculated on the assumption that the methoxide ion is solvated by three methanol molecules. The three plots for each dinitrobenzene were practically identical indicating that the second-order rate constants were independent of what cation (Li^+, Na^+, or K^+) was present in the reaction solution. The plots of unit slope are impressive but the possibility of their being fortuitous cannot be excluded, particularly in view of the results of the correlations of reaction rate with H_M by More O'Ferrall and Ridd, the apparent existence of several H_M scales, and the observation that the dinitrobenzene rates and the dinitroanisole indicator ratios do not show the same dependence on acidity function.

5. Acidity Functions for Alcohol–Alkoxide–Dimethyl Sulphoxide Mixtures

The basicity of alcoholic alkoxide and aqueous hydroxide solutions is greatly enhanced by the addition of dimethyl sulphoxide. Thus measurement of the ionisation of substituted anilines and diphenlyamines in methanol-dimethyl sulphoxide mixtures containing 0·025M-sodium methoxide gave an H_- acidity function which ranged from *ca.* 12 in 100% methanol to *ca.* 19 in 95% dimethyl sulphoxide.[34] It has been argued that this enormous increase in basicity results from an increase in methoxide activity owing to competition between methoxide ions and dimethyl sulphoxide for the solvent methanol. Thus increasing the dimethyl sulphoxide concentration leads to a less hydrogen bonded, more reactive methoxide species.

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[33] R. Schaal and F. Peuré, *Compt. rend.*, 1963, **256**, 4020; *Bull. Soc. chim. France*, 1963, 2638; R. Schaal and J-C. Latour, *ibid.*, 1964, 2177.

[34] R. Stewart, J. P. O'Donnell, D. J. Cram, and B. Rickborn, *Tetrahedron*, 1962, **18**, 917.

Since acid ionisation constants of the indicators in water were used to deduce the acidity function, an H_- scale (standard state, water) was defined. This deviates from the H_M scale (standard state, methanol) according to $(H_M - H_-) = pK_a(\text{MeOH}) - pK_a(\text{HOH})$, where $pK_a(\text{MeOH})$ and $pK_a(\text{HOH})$ are the acid ionisation constants of a particular indicator in methanol and water respectively. It follows that for a series of indicators to give a unique H_- scale in methanol solutions both (f_{AH}/f_{A^-}) for a particular solution and $pK_a(\text{MeOH}) - pK_a(\text{HOH})$ must be independent of indicator. Furthermore, only if these criteria apply will deduction by the stepwise procedure of $pK_a(\text{HOH})$ from measurements on methanol solutions give true thermodynamic equilibrium constants referred to water as the standard state.

The rates of racemisation of (+)-2-methyl-3-phenylpropionitrile in the same base media paralleled the H_- scale ($\log_{10}k_{\text{obs}}$ was linear in H_-; slope 0·87) over a 10^6 variation in rate constant.[34] Two possible mechanisms for the racemisation can be represented by Scheme 2, where k_2 and $k_{-1} \gg k_1$ and for mechanism (*a*) $k_{-1} \gg k_2$ whereas for mechanism (*b*) $k_2 \gg k_{-1}$.

SCHEME 2

$$\begin{array}{ccccccc} \text{AH} + \text{OMe}^- & \underset{-1}{\overset{1}{\rightleftharpoons}} & \text{A}^-\text{....HOMe} & \xrightarrow{2} & \text{A}^-\text{....HOMe} & \xrightarrow{-1} & \text{AH....OMe}^- \\ \begin{array}{c}\text{optically}\\ \text{active}\end{array} & & \begin{array}{c}\text{optically}\\ \text{active}\end{array} & & \text{racemic} & & \text{racemic} \end{array} \qquad (29)$$

Comparison of the probable structures of the transition states for the two mechanisms with the corresponding structure of the anions of the H_- indicators led to the conclusion that the H_- dependence is consistent with mechanism (*a*). This conclusion is in accord with the observed H_M dependencies of the rates of methanolysis of chloroform and phenethyl chloride.[31] Many S_N2 reactions involving alkoxide ions as nucleophiles also show large increases in reaction rate on addition of dimethyl sulphoxide to the solvent.[35]

Bowden and Stewart have established an H_- scale for ethanolic dimethyl sulphoxide containing 0·01M-sodium ethoxide using carbon acids (*i.e.*, acids in which the ionisable hydrogen atom is bonded to carbon) as indicators.[36] The scale closely parallels that for nitrogen acids in methanolic dimethyl sulphoxide and this suggests that the anions of the two types of acid indicator have similar solvation patterns.

6. Acidity Functions for Some Other Basic Media

The effect of dimethyl sulphoxide on basicity is not unique. Experimental H_- scales for the systems phenyltrimethylammonium hydroxide–water–

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[35] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163; C. A. Kingsbury, *J. Org. Chem.*, 1964, **29**, 3262.

[36] K. Bowden and R. Stewart, *Tetrahedron*, 1965, **21**, 261.

sulpholan,[37] tetramethylammonium hydroxide–water–pyridine,[8] tetramethylammonium hydroxide–water–sulpholan,[8] ethanolamine–water,[38] ethylenediamine–water,[39] and hydrazine–water,[40] show that sulpholan, pyridine, ethanolamine (2-aminoethanol), ethylenediamine, and hydrazine have a similar effect. The basicity of the last three is such that the addition of further strong base to the solvent system is unnecessary as they themselves generate sufficient hydroxide ions in aqueous solution. It should be noted that for solutions containing a high proportion of a solvent with a low dielectric constant, ion association is likely, and therefore spectrophotometric measurements of indicator equilibria in mixed solvents are often difficult to interpret.

Comparison of the rates of reaction of *p*-dinitrobenzene and 1-chloro-2,4-dinitrobenzene in aqueous ethylenediamine show that whereas for the former $\log_{10}k_{\text{obs}}$ is linear (slope 1·3) in the logarithm of the stoicheiometric ethylenediamine concentration, for the latter $\log_{10}k_{\text{obs}}$ is linear (slope 0·7) in H_-.[41] The exact mechanistic significance of this has not been discussed.

7. The Determination of pK_a for Weak Acids by Use of the Acidity Function Concept

Indicator studies of strongly basic solvent systems provide as a corollary information about the acidity of the indicators themselves. Acidity function measurements provide an important method for the determination of the ionisation constants of weak acids, and the effect of substituents on the acidity of indicator molecules. Thus the changes with ring substituents of the acidity of anilines and diphenylamines in water are similar to the changes for the corresponding phenols.[42] Furthermore the acid ionisation constants of the neutral anilines and diphenylamines (pK_a) and of their conjugate acids (pK_{BH^+}, evaluated from indicator measurements of the protonation of the neutral amines in concentrated acid solution) show similar trends, a plot of pK_a against pK_{BH^+} being linear[42] with slope 0·6. Changes in ionisation behaviour and ionisation constants of weak acids in passing from one solvent to another can provide valuable information of activity-coefficient behaviour and solvation requirements of the acids and their conjugate bases in the different solvents. Thus comparison of the acidities of a series of t-butylphenols in methanol and water suggest the possibility that bulky substituents *ortho* to the hydroxy-group inhibit solvation of the phenoxide ions.[24,25] Ionisation constants in water up to pK_a=34·1 (diphenylmethane) have recently been deduced for several very

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[37] C. H. Langford and R. L. Burwell, *J. Amer. Chem. Soc.*, 1960, **82,** 1503.
[38] F. Masure and R. Schaal, *Bull. Soc. chim. France*, 1956, 1138.
[39] R. Schaal, *Compt. rend.*, 1954, **238,** 2156.
[40] N. C. Deno, *J. Amer. Chem. Soc.*, 1952, **74,** 2039.
[41] C. Jacquinot-Vermesse and R. Schaal, *Compt. rend.*, 1964, **258,** 2334.
[42] R. Stewart and J. P. O'Donnell, *Canad. J. Chem.*, 1964, **42,** 1694.

weak carbon acids by use of the stepwise acidity function procedure.[43,44] It is important to note that these results rely on the assumptions that the change in acid ionisation constant in going from water to another solvent is independent of indicator, that for a given base solution (f_{SH}/f_{S^-}) is the same for all the indicators in the series, and that none of the indicators ionises by base addition. Proof that an indicator colour change refers to a base addition rather than a proton transfer reaction can sometimes be obtained by n.m.r. spectroscopy.[3]

Arnett has reviewed the evaluation of dissociation constants from studies of the ionisation equilibria of weak bases in concentrated acid solutions.[45]

8. Conclusion

The original concept that, providing the relevant ionisation occurred, a particular acidity function was independent of the class of indicator used to measure it, has been proved incorrect. This makes the use of acidity functions as a criterion of mechanism reliant upon knowledge of the variation of reaction rate with acidity function for reactions of known mechanism. In particular to assign a mechanism to a given reaction, a series of reactions conforming to the possible alternatives must previously have been studied. Present data are sparse but do suggest that it may be possible to deduce valuable information concerning the extent of solvation and of bond making or breaking at the transition state of measurably fast reactions. Also solvation requirements of weak acids and their conjugate bases can be inferred from equilibrium studies. However knowledge of the behaviour of solute activity coefficients in concentrated base solutions is small. Until this deficiency is remedied the possibility that conclusions drawn from acidity function data (particularly with regard to solvation) are spurious cannot be rejected. The determination of ionisation constants of weak acids remains an important application of acidity functions.

In this Review only reactions between neutral indicator molecules and base have been considered. Proton loss from or base addition to charged solute species require the definition of still more acidity functions not necessarily numerically identical to their neutral indicator counterparts. Few results for such functions are available.[32,46]

The author thanks Professor V. Gold for criticism and advice during the preparation of this Review.

[43] E. C. Steiner and J. M. Gilbert, *J. Amer. Chem. Soc.*, 1965, **87**, 382.

[44] A. Streitwieser, J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *J. Amer. Chem. Soc.*, 1965, **87**, 384.

[45] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.

[46] K. Bowden, A. Buckley, and R. Stewart, *J. Amer. Chem. Soc.*, 1966, **88**, 947.