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ACIDITY FUNCTIONS—IX[1]

THE PREPARATION OF BUFFERED SOLUTIONS OF DEFINED BASICITY IN ABSOLUTE METHANOL

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Abstract—Ionisation data for a series of phenol indicators are used to define H_m values for non buffered (H_m 16·4–13·9), phosphate buffered (14·0–12·2) and borate buffered (13·5–11·2) solutions of tetramethylammonium hydroxide and methoxide mixture in methanol. The dissociation constants of the phenols in methanol are also reported.

The preparation of buffered solutions of defined basicity is of fundamental importance in many areas of pure and applied chemistry. For the study of kinetics or equilibria in the absence of water, methanol often represents a very suitable protic solvent and in connection with such studies we required media of defined basicity in the range H_m 10–16.[2] Acidity functions in absolute methanol have been defined for strongly basic media ($H_m > ca.$ 15),[3-7] while for weakly basic solutions (5·4–6·8) the use of HCl/NaCl has been described as a buffering system.[8] In the region 9·6–17·8, Rochester and Rossall have used phenols/phenolates as buffers,[9] but our requirement that the medium should not absorb in the UV precluded the application of this type of system. The present paper reports the use of phosphate and borate buffers, and the construction of a basicity scale using ionisation data for a series of phenol indicators.

RESULTS AND DISCUSSION

The salts of phosphoric and boric acids are widely used in buffering systems in aqueous media but the use of the sodium and potassium salts in methanol is ruled out on solubility grounds. Accordingly we investigated the more soluble tetramethylammonium salts using as base the product of the reaction of tetramethylammonium bromide with silver oxide in methanol (TMAH/M),† the disadvantage of traces of hydroxide ions being offset by the ease (relative to the use of pure tetramethylammonium methoxide) of preparing reproducible solutions (see Experimental).

$$H_m = pK_{HA} - \log([HA]/[A^-]) \tag{1}$$

$$H_m = \log[^-OMe] + pK_{MeOH} + \log\left[\frac{f_{HA} - f_{OMe}}{f_{A^-} \cdot a_{MeOH}}\right] \tag{2}$$

$$H_m = pK_{MeOH} + \log[TMAH/M]. \tag{3}$$

To anchor the scale for buffered media we first defined the basicity for non buffered solutions. The H_m function measures the ability of basic methanolic media to ionize an acid HA to the anion A^- and is defined by eqn (1).[5,10] The relationship of H_m to base concentration is given[4] by eqn (2) where pK_{MeOH}, the autoprotolysis constant,[3,5] equals 16·92 mole^2 l^{-2} at 25° and activity coefficients, f, refer to methanol as standard state. The deviation of H_m from $\log[^-OMe] + pK_{MeOH}$ is marked above 1M MeO^- but the terms become identical at very low methoxide concentration.[4] In this study, for non buffered solutions containing up to *ca.* 0·01 mole TMAH/M, we describe H_m by eqn (3). Both phenol and *p*-chlorophenol ionise in solutions containing 0·001 to 0·01 mole TMAH/M, and plots of log I against H_m (where $I = [ArO^-]/[ArOH]$) for these indicators are linear with slopes of 1·03, correlation coefficient $n = 0·995$, and 1·06 $n = 0·997$, respectively (Fig. 1). The near unit slopes and the satisfactory agreement between the derived pK_a value for phenol with those reported elsewhere (Table 1), bear out our contention that in this range of basicity eqn (3) approximates closely to the more rigorous eqn (2).

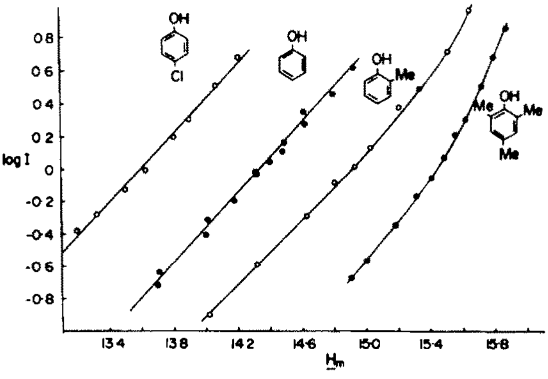

Fig. 1. Plots of log I data against H_m of unbuffered methanol solutions, where $H_m = pK_{MeOH} + \log[TMAH/M]$ (see text).

Plots of log I vs H_m (as defined by eqn 3) for 2-methyl- and 2,4,6-trimethylphenol show a degree of curvature in the plots above *ca.* $H_m = 15·0$ which points to a breakdown of eqn (3) in this region (see Fig. 1). However the plots, though curved, are parallel and the Hammett overlap procedure[11] was applied to log I data measured in solutions of greater base strength than 0·01M TMAH/M. This treatment provided refined H_m data for $H_m > 15·2$ and these are incorporated into Table 2.

To define the H_m function for buffered media of weak basicity we followed the ionisation of 4-chlorophenol in

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†The stoiciometric equation for the reaction defines the base as a 1:1 mixture of tetramethylammonium hydroxide (TMAH) and tetramethylammonium methoxide (TMAM). Hereafter we refer to the base as TMAH/M.

Table 1. pK_a data for phenol indicators in methanol and water

Indicator	pK_a (MeOH)	pK_a (H_2O)[a]
4-Bromo-2-chlorophenol	12.14	7.64[b]
2-Chloro-4-phenylphenol	12.70	8.07[b]
2-Chlorophenol	13.10	8.52
3-Bromophenol	13.30	9.03
4-Chlorophenol	13.59	9.40
Phenol	14.33[c]	9.97
2-Methylphenol	14.90	10.33
2,4,6-Trimethylphenol	15.53	10.89

[a] Values obtained from $\Delta G°$ data collected by J. F. Coetzee and C. D. Ritchie in *Solute Solvent Interactions*, p. 12. Marcel Dekker, London (1969) (except for *b* below).

[b] H. N. Simpson, C. K. Hancock and E. A. Meyers, *J. Org. Chem.* **30**, 2678 (1965).

[c] Error ± 0·05 quoted as standard deviation of points in log *I* plot. *cf* 14·2 obtained using an EMF method [B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac and A. J. Parker, *J. Am. Chem. Soc.* **88**, 1911 (1966)]; 14·46 obtained by a treatment based on eqn (2) (Ref. 6 and corrected in Ref. 9); 14·46 obtained by the overlap method using various phenol/phenolate pairs as buffers (Ref. 9); 14·36 obtained using a refined treatment of the data in Refs. 6, 9 [P. D. Bolton, C. H. Rochester and B. Rossall, *Trans. Faraday Soc.* **66**, 1348 (1970)].

Table 2. H_m values for unbuffered solutions of tetramethylammonium hydroxide/methoxide in methanol (TMAH/M)

Normality of TMAH/M × 10^{-4}	H_m
9.6	13.90[a]
12.0	14.00[a]
38.2	14.50[a]
120.2	15.00[a]
189.9	15.27[b]
253.2	15.38[b]
379.8	15.60[b]
506.4	15.85[b]
633.0	16.18[b]
847.7	16.37[b]

[a] Calculated using eqn (3) (see text).

[b] Calculated using the Hammett overlap procedure.

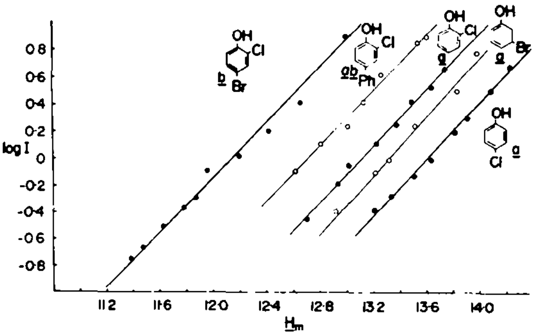

Fig. 2. Plots of log *I* data against H_m values for phosphate buffered media: *a* denotes measurements of indicators in phosphate buffers, *b*, measurements in borate buffers.

Table 3. H_m values for solutions containing 0·02M boric acid or 0·02M phosphoric acid

0.02M Boric acid		0.02M Phosphoric acid	
Normality of TMAH/M	H_m	Normality of TMAH/M	H_m
0.0062	11.17	0.0188	12.25
0.0080	11.50	0.0195	12.50
0.0105	11.75	0.0212	12.75
0.0130	12.00	0.0232	13.00
0.0153	12.25	0.0256	13.25
0.0171	12.50	0.0285	13.50
0.0180	12.75	0.0313	13.75
0.0190	13.00	0.0342	14.00
0.0194	13.25		
0.0200	13.50		

phosphate buffered solutions. By referring the measured log *I* values to those obtained for this indicator in non buffered media, H_m values were assigned to the buffered solutions. With the scale in phosphate buffer now anchored it was extended by applying the overlap procedure to ionisation data for 3-bromophenol, 2-chlorophenol and 2-chloro-4-phenylphenol. Log *I* values for the last of these phenols served to anchor the scale for the borate buffered media where the scale was extended using 4-bromo-2-chlorophenol. The degree of overlap of the log *I* vs base concentration plots is indicated in Fig. 2. H_m values of the buffered media extend over the range 11·2–14·00 (Table 3).

The pK_a values of the phenols in methanol available from this study are compared with literature values obtained for both methanol and aqueous media in Table 1. As is evident from previous studies e.g. Ref.[9], phenols are weaker acids in methanol than in water. A plot of the present values of pK_a in methanol against those in water (Table 1) shows that the three phenols bearing no *ortho* substituent fall on a straight line whereas those with an *ortho* group lie above the line. In a study of *ortho* methyl substituted phenols,[6,9] Rochester and Rossall indicated the possibility that the alkyl group inhibits the solvation of phenolate anions and this effect should become more apparent in the bulkier solvent. Such an effect may account, at least in part, for the non linearity found in this study.

EXPERIMENTAL

Materials. The indicators used were commercial samples and were recrystallized or distilled until the m.p. or b.p. was in agreement with literature values.

Preparation of basic media. Analar grade MeOH was dried by the Mg-method,[12] and flushed with nitrogen for 20 min. Subsequent manipulations were performed under dry N_2 in a dry box. Tetramethylammonium bromide (0·04 mole) and anhy Ag_2O (0·02 mole) were allowed to stand with occasional shaking in MeOH (*ca.* 25 ml) for 30 min. The soln was filtered and the residue washed with a little MeOH (*ca.* 10 ml). The normality of the combined MeOH soln was usually *ca.* 1–1·5N and was standardised by titration with standard HCl using phenolphthalein indicator.

UV measurements. All the stock solns were measured out using 1·00 ml graduated syringes, accurate to 0·01 ml. A typical procedure for making up a soln of a phenol for UV measurement was as follows. 50 ml of a stock soln of the phenol was made up in the dry box, of a concentration 10 times that required for the measurement. A stock soln of TMAH/M was also made up as above, and a soln of buffering agent, if used, at 10 times the required concentrations. 1·0 ml each of the phenol soln and the buffer soln were measured out with the 1·00 ml syringes and introduced into a 10 ml volumetric flask. The appropriate amount of the TMAH/M soln was then measured out with the syringe and introduced into the flask. A 5·0 ml volumetric flask was used for the reference soln, half the quantity of TMAH/M and buffer soln being measured out and added to the 5 ml flask. Both flasks were then made up to the mark with anhyd MeOH. The solns were then transferred to the appropriate UV cells by means of a pipette, which was first flushed out several times with the soln to ensure accuracy. The UV measurements were then immediately recorded using a Unicam SP500 UV spectrophotometer.

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