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NOTE

Effects of Alkali Sulfates and Organic Solvents on the H_0 Function of 70% H_2SO_4/H_2O Mixtures

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In the present work, we have studied the effect of adding alkali sulphates and organic solvents on H_0 of H_2SO_4/H_2O mixtures.

Hammett *et al*[1,2] were pioneers in evaluating the ability of very strongly acidic media to donate protons to indicator bases (B) of varying basicities. This ability is now described as the acidity function (H_0) of the strongly acidic medium. Equation (1) summarises the protonation:

$$B + H^+ = BH^+ \quad (1)$$

Equation (1) can be written in the alternative form:

$$H_0 = pK^+_{BH} - \log (BH^+)/(B) \quad (2)$$

where H_0 = the acidity function of the strongly acidic medium, $pK^+_{BH} = -\log K^+_{BH}$ = the indicator acidity constant of the protonated base and (BH^+) and (B) are the molar concentrations of the protonated and unprotonated bases so that (B) = (B_0) – (BH^+).

Equation (2) is used[3] to find pK^+_{BH} for any suitable indicator base in an acidic solution of known H_0. It is also used to find the acidity function H_0 when pK^+_{BH} for the indicator base is known[3–9].

An aim of this work was to study the effect of adding alkali sulfates or organic solvents on H_0 of H_2SO_4/H_2O mixtures at 70% H_2SO_4 whose $H_0 = 5.67$.

A set of methoxybenzophenone indicators was used which were; 2,2′,4,4′-tetramethoxybenzophenone (TMB), 2,4,4′-trimethoxybenzophenone (TriMB), 4,4′-dimethoxybenzophenone (DMB) and 4-OH-benzophenone (4-OHB).

Solutions of H_2SO_4/H_2O mixtures were prepared by standard analytical procedures. The H_0 function was taken from reference 3.

A UV/Vis Bosch and Lomb model 2000 thermally controlled spectrophotometer was used with matched silica cells.

Solutions of all derivatives of benzophenone indicators were prepared by

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weight in absolute ethanol. A fixed amount of the indicator was dried under vacuum in a 25 mL measuring flask which was then filled with the H_2SO_4/H_2O mixture to find the absorbance of the BH^+ species, its concentration in mol/L of the indicator and its pK^+_{BH}. Table-1 includes the pK^+_{BH} values of the indicators.

TABLE-1
pK^+_{BH} VALUES OF TMB, TriMB, DMB AND 4-OHB IN H_2SO_4/H_2O MIXTURES AT 298 K

TMB	TriMB	DMB	4-OHB
3.065 ± 0.10	3.468 ± 0.11	4.259 ± 0.07	4.830 ± 0.12

The alkali sulfates added were $(NH_4)_2SO_4$, Na_2SO_4 and Li_2SO_4. A known weight of the sulfate was added to the 70% H_2SO_4/H_2O in the reference flask and an equal amount was added to another sample which contained a fixed amount of the indicator base. Solution absorbances were recorded after each sulfate addition. A maximum sulfate concentration at 3.0 mol/L was reached in the each case and the H_0 function was evaluated and the data are given in Table 2.

TABLE-2
H_0 VALUES OF H_2SO_4/H_2O MIXTURES AT 70% H_2SO_4 AT 298 K AND 3.0 mol/L SULFATE CONCENTRATION

H_0	TMB	TriMB	DMB	4-OHB
(Salt) = 0	5.670	5.670	5.670	5.670
$(NH_4)_2SO_4$ at 3.0 mol/l	2.523	2.911	3.533	4.267
Na_2SO_4 at 3.0 mol/l	2.514	3.015	3.572	4.090
Li_2SO_4 at 3.0 mol/l	2.556	2.924	3.267	4.252
Mean H_0 value	2.513	2.950	3.593	2.243
ΔH_0	3.140	2.720	2.080	1.430

Organic solvents added to H_2SO_4/H_2O mixtures were dimethylformamide (DMFA), dimethylsulfoxide (DMSO), ethanol (EtOH), and methanol (MeOH).

For all measurements involving organic solvents the amount of H_2SO_4 was kept unchanged at 70% of the system. Equal amounts of organic solvents were added to the reference solvent and to the experimental solution which contains the indicator base and is used to find H_0 of the system. The H_0 data are given in Tables 3 A and 3B.

TABLE-3A
H_0 VALUES OF 70% H_2SO_4/H_2O TO WHICH ORGANIC SOLVENTS WERE ADDED AT 298 K AND TMB AS INDICATOR

(Water)/(Organic Solvent)	DMFA	DMSO	EtOH	MeOH
(Water)/0	5.670	5.670	5.670	5.670
3/1	3.734	3.433	3.618	3.730
1/1	3.535	3.200	3.382	3.618

TABLE-3B
H_0 VALUES OF 70% H_2SO_4 TO WHICH ORGANIC SOLVENTS WAS ADDED AND CONTAINS NO WATER AT 298K

	DMFA	DMSO	EtOH	MeOH
TMB	2.971	2.786	3.290	3.281
TriMB	4.144	4.151	4.004	4.074
DMB	4.360	4.382	4.441	4.680
4—OHB	4.979	4.813	4.953	4.955

The Basic Nature of Indicator Bases:

Table-1 shows a display of the pK^+_{BH} values of methoxybenzophenone indicators used and which range from 3.065 for TMB to 4.83 for 4-OHB. They become fully protonated over varying H_2SO_4/H_2O mixtures. Table-4 includes the acid ranges suitable for the full protonation of such indicators.

TABLE-4
H_2SO_4 CONCENTRATION RANGES FOR FULL PROTONATION OF METHOXYBENZOPHENONE INDICATORS AT 298K

TMB	TriMB	DMB	4-OHB
40–60%	45–65%	50–70%	60–75%

The data in Table-4 show overlapping behaviour towards H_0 changes of H_2SO_4/H_2O mixtures in which TMB illustrates maximum sensitivity towards such H_0 changes while 4-OHB has a minimum sesitivity which justifies considering the H_0 data for TMB as basic for describing and interpreting the H_0 data.

The Basis Nature of Alkali Sulfates and Organic Solvents in H_2SO_4/H_2O Mixtures

The effects of adding alkali sulfates and organic solvents to H_2SO_4/H_2O mixtures are shown by the H_0 data in Table-2 and Tables 3A and 3B. The overall picture shows that such additions cause a decrease in the numerical value of H_0 suggesting that the system, in all cases, became more basic[3–9]

For alkali sulfates H_0 changed from 5.67 to 2.53 (at 3.0 mol/L alkali sulfate and TMB indicator) It also changed from 5.67 to 3.08 for organic solvents and TMB indicator.

To reationalise such changes in acidity function of H_2SO_4/H_2O mixtures we may consider the behaviour of solutes in this system.

Alkali sulfates ionise in a rather simple manner[10] as they all give rise to the HSO_4^- anion which stimulates the OH^- ion in water[10]

$$M_2SO_4 + H_2SO_4 = 2M^+ + 2HSO_4^- \quad (3)$$

$$MOH \text{ (in water)} = M^+ + OH^- \quad (4)$$

Addition of DMFA, DMSO, EtOH and MeOH to H_2SO_4/H_2O mixtures may

be described as a three component system which includes two competing bases (H_2O and organic baes) and H_2SO_4. Both water and the organic solvents used in this work ionise in sulfuric acid according to the equations (5) and (6).[10]

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad (5)$$

$$\text{(Organic solvent)} \qquad B + H_2SO_4 = BH^+ + HSO_4^- \quad (6)$$

Equations (3), (5) and (6) give rise to the HSO_4^- anion which accounts for the increased basic trend in the H_2SO_4/H_2O mixture at 70% H_2SO_4.

The average H_0 values in Table-2 and 3B for TMB indicator are found to be 2.53 for alkali sulfates and 3.08 for organic solvents which throws light on their basic behaviour. The lower H_0 value for alkali sulfates suggests a stronger basic character for sulfates in H_2SO_4/H_2O than that shown by organic solvents. This might be explained by the full ionisation of sulfates[10] while organic solvents are not fully protonated in the presence or absence of water[10–12]

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