Acid–Base Indicators: Transition Colours and pH Ranges Determined in Select Aqueous–Organic Mixed Solvents

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Transition colours and pH ranges are reported for nine acid–base indicators dissolved in selected aqueous–methanol and aqueous-1,4-dioxane solvent mixtures.

Keywords: Acid–base indicators; transition colour; mixed solvent; pH *range*

Introduction

Acid–base titrations in neat organic and binary aqueous–organic solvent mixtures have been used successfully in analysing acids or bases that either have limited water solubility or are too weakly acidic or basic in aqueous solution to permit accurate end-point detection. Over the past two decades individual researchers,[1–10] as well as scientific organizations,[1,11] have addressed the issue of pH determinations in non-aqueous solvents. As representative examples, Covington[1] discussed existing multi-standard pH scales and the need to adopt standard procedures at both the national and international levels. The International Union of Pure and Applied Chemistry established criteria for standardization of pH measurements, and published recommended pH values for standard reference solutions for methanol, 1,4-dioxane, dimethyl sulfoxide, aqueous–methanol, aqueous–ethanol and aqueous–dimethyl sulfoxide mixed solvents at various temperatures.[11] Mussini and co-workers[3–5] reported standard pH values for potassium hydrogen phthalate reference buffers in select aqueous–organic mixtures. Roy *et al.*[6] determined acid dissociation constants and pH values for standard *N,N*-bis(2-hydroxyethyl)-2-aminoethane sulfonic acid (Bes) and *N*-tris(hydroxymethyl)methylglycine (Tricine) buffer solutions in three aqueous–dimethyl sulfoxide mixtures between −25 and 25 °C. More recently, and from a more theoretical standpoint, Bosch and co-workers [7,8,10] and Rosés and co-workers[9] studied ionic equilibria in amphiprotic solvents of low relative permittivity constant, and derived equations to enable pH computations in solutions of acids, bases, salts and their mixtures. The authors also derived expressions for constructing titration curves of monoprotic and diprotic bases in glacial acetic acid, and for defining autoprotolysis in aqueous–organic solvent mixtures.

Studies involving acid–base indicators have been limited for the most part to the more common neat organic solvents.[12–17] Barbosa *et al.*[12] examined the applicability of 1,4-dihydroxyanthraquinone as an acid–base indicator in propan-2-ol. Calatayud *et al.*[13] screened Crystal Violet, Methyl Violet, Tropaeolin 00, Bromocresol Purple and Malachite Green for perchloric acid titrations in acetic acid. Barbosa *et al.*[14] reviewed parameters of recommended indicators for non-aqueous titrations performed in acetic acid, acetonitrile, propan-2-ol and *tert*-butanol. There has not been, to our knowledge, a systematic investigation of pH indicator behaviour in mixed aqueous–organic solvents. To address this concern, we report pH ranges and the corresponding transition colours of several common acid–base indicators for binary aqueous–methanol (10, 20 and 50% m/m methanol) and aqueous-1,4-dioxane (10, 30 and 50% m/m dioxane). These measurements extend our preliminary study[18] involving indicator behaviour in aqueous–methanol (50% m/m methanol) and aqueous–acetonitrile (30% m/m acetontrile), which was published as part of an undergraduate laboratory experiment.

Experimental

The spectral behaviour of the nine indicators was studied. Methanol (Aldrich, Milwaukee, WI, USA) HPLC Grade, 99.9+% and 1,4-dioxane (Aldrich HPLC Grade, 99.9%) were used as received. Chromatographic analyses showed all purities to be within the manufacturer's specifications. Doubly de-ionized water was used in all mixture preparations, as well as for the neat aqueous solvent. Spectral colour transitions were determined by visual observation after incremental drop-wise addition (both *via* Pasteur pipette and syringe) of perchloric acid or sodium hydroxide solution to about 100 ml of solvent. Solvent composition was maintained constant throughout the measurements. Each perchloric acid and sodium hydroxide solution used was prepared from the solvent mixture being studied. Colour transitions (against a white background) were verified by repetitive measurements, approaching the transition from both the acidic and basic side. Solution pH was calculated from experimental potentiometric measurements in accordance with published procedures.[19] Potentials were determined experimentally with a combination glass-saturated calomel electrode, which had been previously standardized *versus* a 0.05 mol l^{-1} potassium hydrogen phthalate (KHPh) aqueous–organic reference buffer solution.[2–5,19]

Results

Tables 1 and 2 summarize the spectral behaviour of nine select indicators dissolved in the afore-mentioned solvent mixtures. Included for comparison is the behaviour of the indicator in de-ionized water.

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Table 1 Behaviour of acid–base indicators in aqueous–methanol solvent mixtures*

		pH										
Indicators		2	3	4	5	6	7	8	9	10	11	12
Bromocresol Green	Water		Yellow	│	Y–G │				Blue			
	10/90		Yellow	│	Y–G	│			Blue			
	20/80		Yellow	│	Y–G	│			Blue			
	50/50		Yellow		│ Y–G	│			Blue			
Bromocresol Purple	Water		Yellow		│	Y–G │			Blue			
	10/90			Yellow		│ Y–G │				Blue–Purple		
	20/80			Yellow		│ Y–G	│			Blue–Purple		
	50/50				Yellow	│	Y–G	│		Purple		
Bromophenol Blue	Water		Yellow │	Y–G │				Blue				
	10/90		Yellow │	Y–G	│				Blue			
	20/80		Yellow │	Y–G │				Blue				
	50/50		Yellow	│	Yellow–Green		│			Blue		
Bromothymol Blue	Water			Yellow		│	Y–G	│		Blue		
	10/90			Yellow		│	Y–G │			Blue		
	20/80			Yellow		│	Y–G	│		Blue		
	50/50				Yellow		│	Y–G	│	Blue		
Congo Red	Water			Purple	│				Orange			
	10/90		Purple	│ Red │				Orange				
	20/80		Purple	│ Red	│			Orange				
	50/50	P	│				Orange–Red					
Methyl Orange	Water	Red	│	Orange	│				Yellow			
	10/90		Red	│	Orange	│			Yellow			
	20/80		Red	│	Orange	│			Yellow			
	50/50	Red	│	Orange │				Yellow				
Methyl Red	Water		Pink	│	Red	│			Yellow			
	10/90		Pink		│	Orange │			Yellow			
	20/80			Pink		│ Orange	│			Yellow		
	50/50			Pink		│ Orange	│			Yellow		
Methyl Yellow	Water		Red │ O	│				Yellow				
	10/90		Red │	Orange	│			Yellow				
	20/80		Red │	Orange │				Yellow				
	50/50	Red	│ Orange	│				Yellow				
Tumeric	Water				Yellow–Green			│ O │		Brown		
	10/90					Pale Yellow			│		Pale Orange	
	20/80					Pale Yellow			│	Pale Orange		
	50/50					Pale Yellow				│	Pale Orange	

* Colour perception is subjective. Ranges denoted represent the average of eight independent determinations. Abbreviations used: Y–G, yellow–green; O, orange; and P, purple.

Table 2 Behaviour of acid–base indicators in aqueous–1,4-dioxane solvent mixtures*

		pH										
Indicators		2	3	4	5	6	7	8	9	10	11	12
Bromocresol Green	Water		Yellow	│	Y–G │				Blue			
	10/90		Yellow	│	Yellow–Green	│				Blue		
	30/70			Yellow	│ Y–G	│			Blue			
	50/50			Yellow		│	Y–G │			Blue		
Bromocresol Purple	Water			Yellow	│	Y–G │			Blue			
	10/90			Yellow		│ Y–G	│		Blue–Purple			
	30/70			Yellow		│	Y–G	│		Blue–Purple		
Bromophenol Blue	Water		Yellow │	Y–G │				Blue				
	10/90		Yellow │	Y–G	│				Blue			
	30/70		Yellow	│	Y–G │				Blue			
	50/50		Yellow		│	Y–G	│			Blue		
Bromothymol Blue	Water			Yellow		│	Y–G	│		Blue		
	10/90			Yellow			│	Y–G	│	Blue		
	30/70			Yellow			│ G │			Blue		
Congo Red	Water			Purple	│				Orange			
	10/90		Purple │	Red │				Orange				
	30/70		Purple │					Orange				
Methyl Orange	Water	Red	│	Orange	│				Yellow			
	10/90		Red	│	Orange	│			Yellow			
	30/70		Red	│	Orange │				Yellow			
	50/50		Red	│ O │				Yellow				
Methyl Red	Water		Pink	│	Red	│			Yellow			
	10/90			Pink	│	O–R	│		Yellow			
	30/70			Pink		│ R	│			Yellow		
	50/50			Red			│ O │			Yellow		
Methyl Yellow	Water		Red │ O	│				Yellow				
	10/90		Red │	O │				Yellow				
	30/70		O–R │	O–Y │				Yellow				
Tumeric	Water				Yellow–Green			│ O │		Brown		
	10/90				Yellow			│		Orange		
	30/70				Yellow			│		Orange		

* Colour perception is subjective. Ranges denoted represent the average of eight independent determinations. Abbreviations used: Y–G, yellow–green; O, orange; and P, purple.

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