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Determination of the Acidity Constants of Methyl Red and Phenol Red Indicators in Binary Methanol− and Ethanol−Water Mixtures

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The conditional acidity constants, pK_a, of methyl red and phenol red were determined in (10, 30, and 50) wt % binary aqueous mixtures of methanol and ethanol at 298.15 K and at constant low ionic strength ($2.5 \cdot 10^{-3}$ mol·dm^{-3}) by a spectrophotometric method. For methyl red and phenol red and in the studied cosolvent + water systems, pK_a ranged from 3.78 ± 0.06 to 5.50 ± 0.04 and 8.50 ± 0.1 to 6.71 ± 0.03, respectively. Variations in the pK_a of methyl red and phenol red as functions of wt % cosolvents are discussed in terms of solvent properties.

Introduction

In the study of metal−surface reactions in soil systems cocontaminated with nonaqueous and mixed solvents, pH determination is important.[1] pH affects surface reactions directly through its effects on surface charge density and indirectly through its effects on solution properties, namely, complexation and solubility.

Potentiometric and spectrophotometric techniques are both available for pH determination. The method recommended by the IUPAC Commission on Electroanalytical Chemistry is restricted to binary aqueous–organic solvents (e.g., methanol, ethanol, 1,2-ethanediol, etc.) of moderate to high dielectric constant[2] ($\epsilon > 30$) and for which a primary reference value standard, pH$_{PS}$, has been defined.[2–8] These measurements are usually cumbersome and require preconditioning of the pH electrode, the time of which can vary from (10 to 20) days[9] and, at the time of taking readings, require several minutes for the electrode potential to stabilize. Also, these measurements involve nonthermodynamic assumptions such as a constant residual liquid junction potential in solutions of ionic strength different from the standard buffers.[10]

Spectrophotometric techniques using acid–base indicators present an alternative to potentiometric pH methods.[11–13] Because measurements are made via absorbance ratios, pH is directly related to the indicator molecular properties, and calibrating buffers are not required.[14–17] One disadvantage of the spectrophotometric method is the a priori determination of the acidity constants of a particular indicator. Once these constants are calculated, the spectrophotometric method offers a fast, reliable, and accurate method to determine pH.

Although scarce, the thermodynamic equilibrium constants in mixed solvents have been reported for the following indicator dyes: anthraquinones and anthrones in methanol + water,[18,19] alizarine reds[20] in methanol +, ethanol +, dimethylsulfoxide +, and acetonitrile + water, and 4-(2-pyridylazo)resorcinol in methanol + water[21] and in acetonitrile + water.[22]

Table 1. Values of the pH$_{PS}$ of 0.05 mol·kg^{-1} of Potassium Hydrogen Phthalate in Binary Methanol− and Ethanol–Water Mixtures at T = 298.15 K

100 W_1	pH$_{PS}$[a]
Methanol (1) + Water (2)	
0	4.005
10	4.243
30	4.626
50	5.125
Ethanol (1) + Water (2)	
10	4.230
30	4.686
50	5.096

[a] From ref 27. Values that were not available for a specific cosolvent fraction were interpolated from existing data.

In this paper, we determined the conditional acidity constants, pK_a, of two sulfonephthalein acid–base indicators: methyl red (MR) and phenol red (PR) in two cosolvent (methanol and ethanol) + water systems at T = 298.15 K and at low ionic strength. In these and other cosolvent + water systems, the behavior of contaminants has been examined; however, determination of pH has not always been reported,[23] making the interpretation of experimental results difficult.[1] MR and PR are particularly good systems to study acid–base equilibrium in mixed aqueous–organic solvents because both their acid and base forms have strong absorption peaks in the visible portion of the spectrum. In addition, their color change intervals cover a pH range of 4.5 to 8.0, a range where many soil−chemical reactions occur. It is therefore hypothesized that once their pK_a's in mixed aqueous–organic mixtures are determined they can be used by soil scientists in the study of pH in soil solutions cocontaminated with these solvents. In addition, these acidity constants can be used by chemists in analytical procedures such as acid–base titrations, complex formation, and ion transport.[20]

In aqueous solutions, MR (see Scheme 1 for structure) is a zwitterion and has a resonance structure somewhere between the two extreme forms. PR (see Scheme 2 for structure) is a diprotic acid, and it is the color change during the second dissociation reaction that is usually used for indicator acid–base titrations. In aqueous solutions, pH change intervals for MR and PR are 4.5 to 6.0 and 6.5 to 8.0, respectively. These pH

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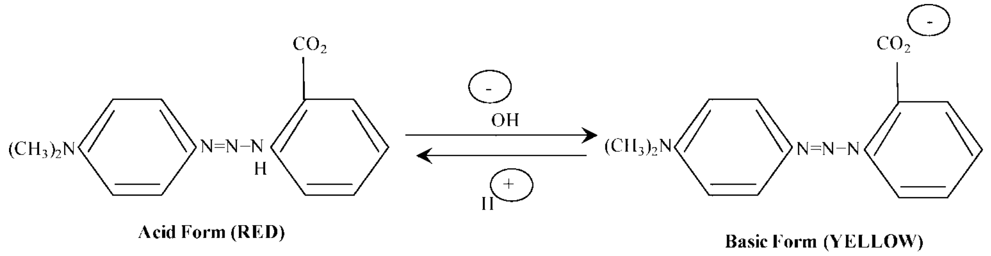
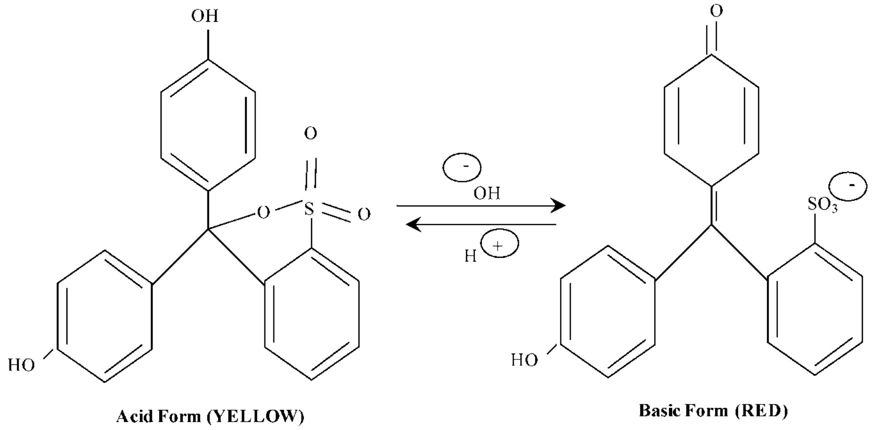
Scheme 1. Chemical Structure of the Acid and Basic Forms of Methyl Red



Scheme 2. Chemical Structure of the Acid and Basic Forms of Phenol Red



ranges can be conveniently obtained using simple acetic acid–sodium acetate (MR) and potassium dihydrogen phosphate–disodium hydrogen phosphate (PR) buffer systems.[24] Studies have been conducted to determine the acid dissociation constants of MR and PR, particularly in highly concentrated (seawater)[14–16] aqueous solutions, and values for their pK_a's have been reported as 5.05 ± 0.05[25] and 7.495 ± 0.006[14] for MR and PR, respectively, at $T = 298.15$ K. These constants are not greatly affected by changes in ionic strength and temperature.[13,14]

Theory. For a generic acid–base indicator HIn

$$\mathrm{HIn} \overset{K_a}{\leftrightarrow} \mathrm{H}^+ + \mathrm{In}^-$$

The acid dissociation constant, K_a, is defined as

$$K_a = \frac{[\mathrm{H}^+][\mathrm{In}^-]}{[\mathrm{HIn}]} \qquad (1)$$

Converting eq 1 into the form of the Henderson–Hasselbach equation, we obtain

$$\mathrm{p}K_a = \mathrm{pH} - \log\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} \qquad (2)$$

In this equation, pH can be measured potentiometrically using the procedure developed by Mussini et al.[2] for organic solvent mixtures of high dielectric constant ($\epsilon > 30$). In this procedure, the relationship between the pH values of an unknown sample (in our case, a series of buffer solutions of varying ratios and constant total ionic strength prepared in cosolvent + water mixtures and containing either MR or PR) and that of a primary reference standard is given by

$$\mathrm{pH} = \mathrm{pH}_{\mathrm{PS}} + \frac{\mathrm{emf}_{(\mathrm{PS})} - \mathrm{emf}_{(\mathrm{unknown\,solution})}}{(\ln 10)(RT/F)} \qquad (3)$$

where emf represents the electromotive force measured in mV, and R, T, and F are the universal gas constant, the absolute temperature in K, and the Faraday constant, respectively.

The ratio [In$^-$]/[HIn] is obtained spectrophotometrically by measuring the absorbance, A, of a solution that contains both forms of an indictor at two wavelengths, λ_{HIn} and λ_{In^-}, according to the following set of equations[13,25]

$$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = \frac{A_{\lambda_{\mathrm{In}^-}}(C_T/A_{\lambda_{\mathrm{In}^-(\mathrm{basic})}})}{A_{\lambda_{\mathrm{HIn}}}(C_T/A_{\lambda_{\mathrm{HIn}(\mathrm{acidic})}})} \qquad (4)$$

or

$$\frac{[\mathrm{In}^-]}{[\mathrm{HIn}]} = \frac{A_{\lambda_{\mathrm{In}^-}}}{A_{\lambda_{\mathrm{HIn}}}} \cdot R_{\mathrm{I}} \text{ with } R_{\mathrm{I}} = \frac{A_{\lambda_{\mathrm{HIn}(\mathrm{acidic})}}}{A_{\lambda_{\mathrm{In}^-(\mathrm{basic})}}} \qquad (5)$$

λ_{HIn} depicts the wavelength at which the acid and not the basic form of the indicator strongly absorbs; λ_{In^-} is where the basic and not the acidic form of the indicator absorbs; and C_T is the total concentration of the indicator.

All the absorbances used in these equations are background corrected such that

$$A^{\mathrm{HIn}}_{\lambda_{\mathrm{HIn}}} = A^{\mathrm{HIn}}_{\lambda_{\mathrm{HIn}}}(\mathrm{measured}) - A^{\mathrm{HIn}}_{\lambda_{\mathrm{In}^-}}(\mathrm{acidic}) \qquad (6)$$

where $A^{\mathrm{HIn}}_{\lambda_{\mathrm{HIn}}}$ is the corrected absorbance; $A^{\mathrm{HIn}}_{\lambda_{\mathrm{HIn}}}$ (measured) is the measured absorbance; and $A^{\mathrm{HIn}}_{\lambda_{\mathrm{HIn}}}$ (acidic) is the absorbance of HIn at λ_{In^-} from the most acidic solution.[26]

Experimental Section

Materials. Extra pure methanol (HPLC grade, CAS: 67-56-1, Fisher Scientific) and reagent grade SDA$_1$ anhydrous ethanol (95.27 %, CAS: 64-17-5, Fisher Scientific) were used as received. Methyl red sodium salt ($C_{15}H_{14}N_3NaO_2$, CAS: 845-10-3, Acros Organic), phenol red sodium salt ($C_{19}H_{13}NaO_5$, CAS: 34427-61-1, Acros Organic), hydrochloric acid (HCl), sodium hydroxide (NaOH), acetic acid (HOAc), sodium acetate (NaOAc), potassium dihydrogen phosphate (KH_2PO_4), and disodium hydrogen phosphate (Na_2HPO_4) were analytical reagent grade commercial products

Table 2. Data for Methyl Red Indicator in Methanol + Water at $T = 298.15$ K and Constant Ionic Strength ($I = 2.5 \cdot 10^{-3}$ mol·dm^{-3})

100 W_1 = 0

ratios of buffer solutions[a]	emf[b]	pH[c]	measured absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	measured absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	corrected absorbance[d] $\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	corrected absorbance[d] $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	log [MR$^-$]/[HMR][e]	pK_a[f]
				Set I[g]				
2	112	4.95	0.1925	0.5109	0.1188	0.4678	−0.1278	5.07
1.5	105.4	5.06	0.2143	0.412	0.1406	0.3689	0.0005	5.06
1	95.7	5.22	0.2575	0.3351	0.1838	0.292	0.2066	5.02
0.5	80.4	5.48	0.3204	0.267	0.2467	0.2239	0.4331	5.05
0.25	61.8	5.80	0.3826	0.117	0.3089	0.0739	0.8891	4.91
0.2	55.5	5.90	0.3714	0.13	0.2977	0.0869	0.8273	5.07
0.1	39	6.18	0.4148	0.1003	0.3411	0.0572	0.9990	5.18
0.05	21.3	6.48	0.4277	0.0537	0.354	0.0106	1.2865	5.19
acidic solution			**0.0737**	**1.1034**		**1.0603**		
basic solution			**0.4351**	**0.0431**	**0.3614**			
R_{MR}					**2.9339**			

100 W_1 = 10

ratios of buffer solutions[a]	emf[b]	pH[c]	measured absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	measured absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	corrected absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	corrected absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	log [MR$^-$]/[HMR][e]	pK_a[f]
				Set I				
2	120.5	3.52	0.1824	0.6527	0.1356	0.6437	−0.2244	3.74
1.5	113.2	3.64	0.209	0.6032	0.1622	0.5942	−0.1184	3.76
1	102.6	3.82	0.2431	0.49	0.1963	0.481	0.0548	3.76
0.5	85	4.12	0.3106	0.3271	0.2638	0.3181	0.3586	3.76
0.25	61	4.52	0.3594	0.1627	0.3126	0.1537	0.7356	3.79
0.2	67	4.42	0.349	0.2027	0.3022	0.1937	0.6255	3.80
0.1	44.1	4.81	0.3965	0.1096	0.3497	0.1006	0.9559	3.85
0.05	28	5.08	0.4109	0.0689	0.3641	0.0599	1.1750	3.90
				Set II				
2	120.1	3.52	0.2007	0.6824	0.1539	0.6734	−0.1890	3.71
1.5	113.5	3.63	0.2275	0.6267	0.1807	0.6177	−0.0818	3.72
1	102.1	3.83	0.2686	0.5195	0.2218	0.5105	0.0900	3.74
0.5	85.3	4.11	0.3247	0.3484	0.2779	0.3394	0.3652	3.75
0.25	61.2	4.52	0.3813	0.1865	0.3345	0.1775	0.7272	3.79
0.2	66.7	4.43	0.3714	0.2189	0.3246	0.2099	0.6414	3.78
0.1	44	4.81	0.4081	0.1133	0.3613	0.1043	0.9916	3.82
0.05	27.1	5.10	0.4192	0.0739	0.3724	0.0649	1.2108	3.88
acidic solution			**0.0468**	**1.0485**		**1.0395**		
basic solution			**0.4139**	**0.0090**	**0.3671**			
R_{MR}					**2.8316**			

100 W_1 = 30

ratios of buffer solutions[a]	emf[b]	pH[c]	measured absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	measured absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	corrected absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	corrected absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	log [MR$^-$]/[HMR][e]	pK_a[f]
				Set I				
2	94.5	3.86	0.2600	0.5952	0.1692	0.5634	−0.0562	3.91
1.5	87	3.98	0.2869	0.5306	0.1961	0.4988	0.0608	3.92
1	76.4	4.16	0.3211	0.4316	0.2303	0.3998	0.2267	3.94
0.5	59.3	4.45	0.3738	0.2868	0.2830	0.2550	0.5114	3.94
0.25	41.3	4.76	0.4124	0.1760	0.3216	0.1442	0.8146	3.94
0.2	35.3	4.86	0.4244	0.1509	0.3336	0.1191	0.9135	3.94
0.1	17.7	5.16	0.4163	0.1761	0.3255	0.1443	0.8195	4.34
0.05	1.4	5.43	0.4422	0.0892	0.3514	0.0574	1.2531	4.18
				Set II				
2	94	3.87	0.2629	0.6030	0.1721	0.5712	−0.0548	3.92
1.5	87.2	3.98	0.2854	0.5276	0.1946	0.4958	0.0600	3.92
1	76.7	4.16	0.3190	0.4374	0.2282	0.4056	0.2164	3.94
0.5	59.7	4.45	0.3723	0.2853	0.2815	0.2535	0.5117	3.93
0.25	41.5	4.75	0.4074	0.1721	0.3166	0.1403	0.8197	3.93
0.2	35.1	4.86	0.4157	0.1483	0.3249	0.1165	0.9116	3.95
0.1	18.4	5.14	0.4268	0.0881	0.3360	0.0563	1.2420	3.90
0.05	1.4	5.43	0.4497	0.0585	0.3589	0.0267	1.5947	3.84
acidic solution			**0.0908**	**1.1040**		**1.0722**		
basic solution			**0.4573**	**0.0318**	**0.3665**			
R_{MR}					**2.9255**			

100 W_1 = 50

ratios of buffer solutions[a]	emf[b]	pH[c]	measured absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	measured absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	corrected absorbance $\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	corrected absorbance $\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	log [MR$^-$]/[HMR][e]	pK_a[f]
				Set I				
2	66.6	5.57	0.3142	0.4671	0.2089	0.4447	0.1024	5.47
1.5	59.1	5.70	0.3403	0.4140	0.2350	0.3916	0.2088	5.49
1	48.3	5.88	0.3722	0.3310	0.2669	0.3086	0.3675	5.52
0.5	31.6	6.17	0.4077	0.2099	0.3024	0.1875	0.6382	5.53

Table 2 Continued

			100 $W_1 = 50$					
			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	$\lambda_{\mathrm{MR}^-}^{\mathrm{MR}^-}$	$\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	$\lambda_{\mathrm{MR}^-}^{\mathrm{MR}^-}$	log [MR⁻]/[HMR][e]	pK_a[f]
0.25	6.9	6.58	0.4458	0.1069	0.3405	0.0845	1.0358	5.55
0.2	14	6.46	0.4350	0.1272	0.3297	0.1048	0.9283	5.54
0.1	−9	6.85	0.4590	0.0667	0.3537	0.0443	1.3328	5.52
0.05	−26.3	7.15	0.4596	0.0412	0.3543	0.0188	1.7058	5.44
			Set II					
2	67	5.57	0.3235	0.4724	0.2182	0.4500	0.1162	5.45
1.5	59.4	5.70	0.3425	0.4100	0.2372	0.3876	0.2173	5.48
1	48.6	5.88	0.3686	0.3240	0.2633	0.3016	0.3716	5.51
0.5	32.1	6.16	0.4191	0.2123	0.3138	0.1899	0.6487	5.51
0.25	7.5	6.57	0.4472	0.1097	0.3419	0.0873	1.0235	5.55
0.2	13.9	6.47	0.4447	0.1291	0.3394	0.1067	0.9331	5.53
0.1	−9.2	6.86	0.4646	0.0667	0.3593	0.0443	1.3396	5.52
0.05	−25.6	7.13	0.4688	0.0407	0.3635	0.0183	1.7286	5.40
acidic solution			**0.1053**	**1.0169**		**0.9945**		
basic solution			**0.4743**	**0.0224**	**0.3690**			
R_{MR}				**2.6951**				

[a] The buffers used were mixtures of HOAc/NaOAc. [b] emf is the electromotive force measured in mV for each solution. [c] Calculated from eq 3. [d] Corrected absorbance is calculated using eq 6. [e] Calculated using log eq 4. [f] Calculated using eq 2. [g] Each set represents individual replicates.

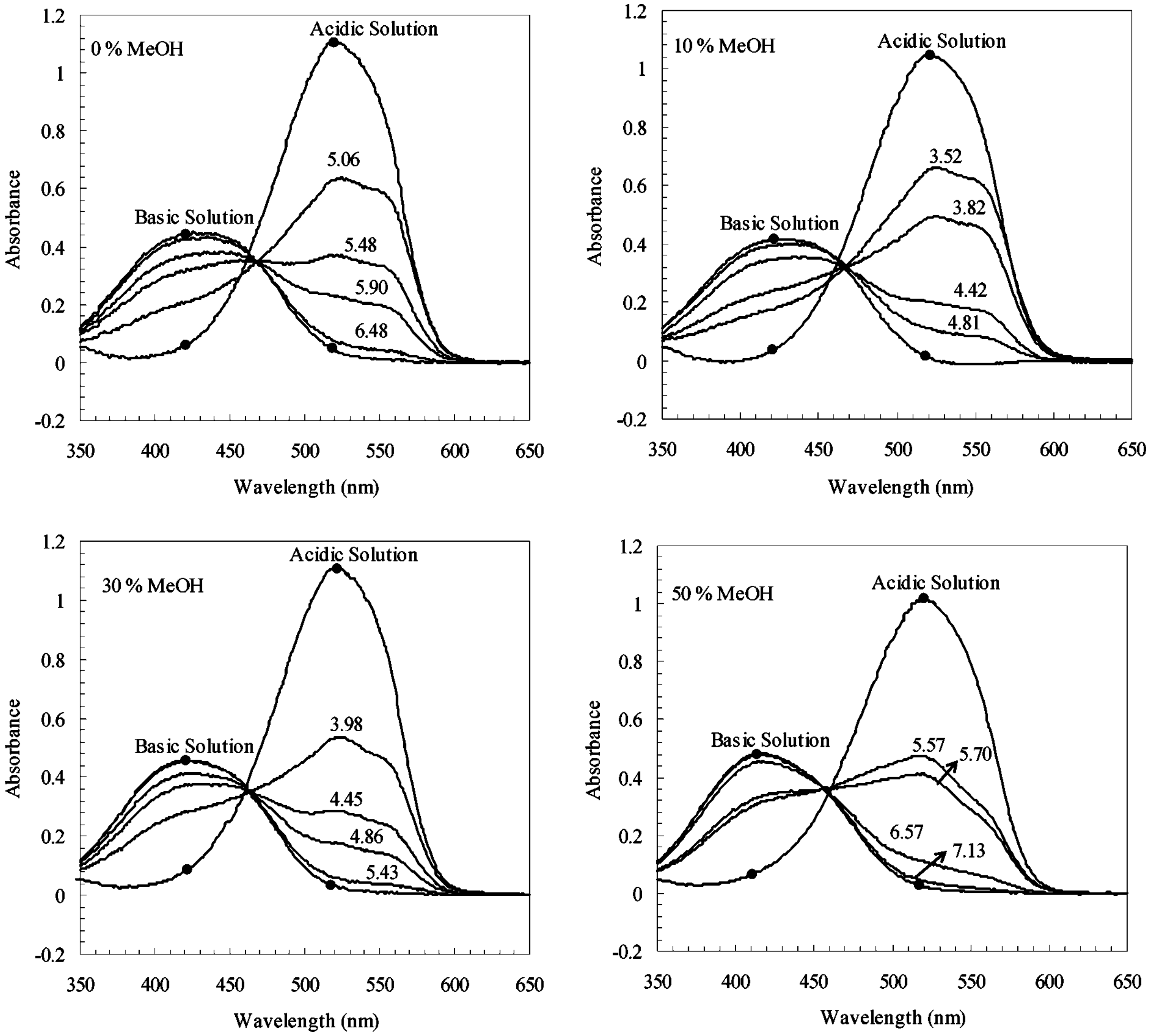


Figure 1. Absorption spectra of methyl red in methanol + water mixtures at $I = 2.5 \cdot 10^{-3}$ mol·dm^{-3} at different pH values (specified by the numbers above the absorption curves).

from Fisher Scientific. All reagents were used without further purification. Standard stock solutions of $5.49 \cdot 10^{-3}$ mol·dm^{-3} MR and $5.31 \cdot 10^{-3}$ mol·dm^{-3} PR were prepared by dissolving appropriate amounts of MR in 95 % ethanol and diluting with distilled water[25] and of PR in distilled water.[24] Working solutions of HCl, NaOH, HOAc, NaOAc, KH_2PO_4, and Na_2HPO_4 were prepared

Table 3. Data for Methyl Red Indicator in Ethanol + Water at $T = 298.15$ K and Constant Ionic Strength ($I = 2.5 \cdot 10^{-3}$ mol·dm^{-3})

100 W_1 = 10

			measured absorbance		corrected absorbance[d]			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	$\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	$\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	$\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	$\log [\mathrm{MR}^-]/[\mathrm{HMR}]$[e]	pK_a[f]
Set I[g]								
2	120.5	4.84	0.1983	0.6855	0.1263	0.6435	−0.2498	5.09
1.5	112.9	4.97	0.2248	0.6272	0.1528	0.5852	−0.1258	5.09
1	102.4	5.14	0.2611	0.5235	0.1891	0.4815	0.0515	5.09
0.5	85.1	5.44	0.3152	0.3573	0.2432	0.3153	0.3446	5.09
0.25	67	5.74	0.3633	0.2295	0.2913	0.1875	0.6487	5.09
0.2	60.9	5.85	0.3747	0.1971	0.3027	0.1551	0.7478	5.10
0.1	43.8	6.14	0.4017	0.1229	0.3297	0.0809	1.0676	5.07
0.05	26.2	6.43	0.4141	0.0795	0.3421	0.0375	1.4175	5.02
Set II								
2	120.5	4.84	0.1931	0.6858	0.1211	0.6438	−0.2682	5.11
1.5	113	4.97	0.2236	0.6232	0.1516	0.5812	−0.1262	5.09
1	102.5	5.14	0.2542	0.5254	0.1822	0.4834	0.0336	5.11
0.5	85.2	5.44	0.3143	0.3568	0.2423	0.3148	0.3437	5.09
0.25	67.3	5.74	0.3583	0.2247	0.2863	0.1827	0.6525	5.09
0.2	60.9	5.85	0.3714	0.1927	0.2994	0.1507	0.7555	5.09
0.1	44	6.13	0.3956	0.1190	0.3236	0.0770	1.0809	5.05
0.05	26.6	6.43	0.4070	0.0778	0.3350	0.0358	1.4285	5.00
acidic solution			**0.0720**	**1.0872**		**1.0452**		
basic solution			**0.4366**	**0.0420**	**0.3646**			
R_{MR}				**2.8667**				

100 W_1 = 30

			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	$\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	$\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	$\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	$\log [\mathrm{MR}^-]/[\mathrm{HMR}]$[e]	pK_a[f]
Set I								
2	91.8	5.15	0.2128	0.6760	0.1349	0.6521	−0.2514	5.40
1.5	84.2	5.28	0.2341	0.6192	0.1562	0.5953	−0.1481	5.43
1	74	5.45	0.2706	0.5372	0.1927	0.5133	0.0074	5.45
0.5	56.7	5.75	0.3166	0.3769	0.2387	0.3530	0.2630	5.48
0.25	38.7	6.05	0.3626	0.2365	0.2847	0.2126	0.5597	5.49
0.2	32.3	6.16	0.3834	0.2052	0.3055	0.1813	0.6595	5.50
0.1	15.5	6.44	0.4147	0.1216	0.3368	0.0977	0.9704	5.47
0.05	−1.6	6.73	0.4294	0.0709	0.3515	0.0470	1.3068	5.42
Set II								
2	92.1	5.15	0.2142	0.6858	0.1363	0.6619	−0.2534	5.40
1.5	84.5	5.28	0.2381	0.6286	0.1602	0.6047	−0.1440	5.42
1	74	5.45	0.2728	0.5433	0.1949	0.5194	0.0072	5.45
0.5	57.2	5.74	0.3222	0.3882	0.2443	0.3643	0.2594	5.48
0.25	38.9	6.05	0.3704	0.2495	0.2925	0.2256	0.5457	5.50
0.2	32.6	6.15	0.3818	0.2132	0.3039	0.1893	0.6385	5.52
0.1	15.8	6.44	0.4145	0.1301	0.3366	0.1062	0.9339	5.50
0.05	−0.9	6.72	0.4305	0.0812	0.3526	0.0573	1.2221	5.50
acidic solution			**0.0779**	**1.0246**		**1.0007**		
basic solution			**0.4472**	**0.0239**	**0.3693**			
R_{MR}				**2.7097**				

100 W_1 = 50

			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HMR}}^{\mathrm{MR}}$	$\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	$\lambda_{\mathrm{HMR}}^{\mathrm{HMR}}$	$\lambda_{\mathrm{MR^-}}^{\mathrm{MR^-}}$	$\log [\mathrm{MR}^-]/[\mathrm{HMR}]$[e]	pK_a[f]
Set I								
2	63.5	5.16	0.2608	0.6113	0.1438	0.5730	−0.1649	5.32
1.5	55.7	5.29	0.2840	0.5651	0.1670	0.5268	−0.0634	5.35
1	45.5	5.47	0.3068	0.4833	0.1898	0.4450	0.0654	5.40
0.5	29.8	5.74	0.3568	0.3511	0.2398	0.3128	0.3201	5.41
0.25	11.3	6.04	0.3882	0.2206	0.2712	0.1823	0.6080	5.43
0.2	4	6.16	0.4036	0.1969	0.2866	0.1586	0.6925	5.47
0.1	−11.7	6.42	0.4301	0.1135	0.3131	0.0752	1.0550	5.38
0.05	−27.4	6.68	0.4454	0.0757	0.3284	0.0374	1.3790	5.32
Set II								
2	63.6	5.16	0.2748	0.6228	0.1578	0.5845	−0.1332	5.29
1.5	56	5.29	0.2794	0.5571	0.1624	0.5188	−0.0689	5.36
1	45.4	5.47	0.3060	0.4808	0.1890	0.4425	0.0660	5.40
0.5	29.3	5.74	0.3579	0.3457	0.2409	0.3074	0.3296	5.41
0.25	11.3	6.04	0.3966	0.2219	0.2796	0.1836	0.6182	5.42
0.2	4.1	6.16	0.4060	0.1887	0.2890	0.1504	0.7192	5.44
0.1	−11.2	6.42	0.4336	0.1146	0.3166	0.0763	1.0535	5.37
0.05	−26.6	6.68	0.4480	0.0724	0.3310	0.0341	1.4226	5.26
acidic solution			**0.1170**	**0.9719**		**0.9336**		
basic solution			**0.4595**	**0.0383**	**0.3425**			
R_{MR}				**2.7258**				

[a] The buffers used were mixtures of HOAc/NaOAc. [b] emf is the electromotive force measured in mV for each solution. [c] Calculated from eq 3. [d] Corrected absorbance is calculated using eq 6. [e] Calculated using log eq 4. [f] Calculated using eq 2. [g] Each set represents individual replicates.

Table 4. Data for Phenol Red Indicator in Methanol + Water at $T = 298.15$ K and Constant Ionic Strength ($I = 2.5 \cdot 10^{-3}$ mol·dm^{-3})

ratios of buffer solutions[a]	emf[b]	pH[c]	measured absorbance		corrected absorbance[d]		log [PR$^-$]/[HPR][e]	pK_a[f]
			$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$		
100 W_1 = 0								
Set I[g]								
4	11.3	6.65	0.3743	0.0392	0.3304	0.0368	−1.4422	8.09
2	−4.2	6.91	0.3634	0.0717	0.3195	0.0693	−1.1532	8.06
1	−20.6	7.19	0.3387	0.1183	0.2948	0.1159	−0.9089	8.10
0.5	−35.8	7.45	0.3117	0.2201	0.2678	0.2177	−0.5853	8.03
0.25	−48.7	7.66	0.2806	0.3111	0.2367	0.3087	−0.3837	8.05
0.2	−50	7.69	0.2922	0.2985	0.2483	0.2961	−0.4090	8.09
0.1	−68.2	7.99	0.221	0.5058	0.1771	0.5034	−0.0401	8.03
0.05	−76.4	8.13	0.1943	0.6021	0.1504	0.5997	0.1192	8.01
acidic solution			**0.3889**	**0.0024**	**0.3450**			
basic solution			**0.0439**	**1.0579**		**1.0555**		
R_{PR}					**0.3270**			
100 W_1 = 10								
			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	log [PR$^-$]/[HPR][e]	pK_a[f]
Set I								
4	11	5.37	0.3694	0.0449	0.3233	0.0448	−1.3517	6.72
2	−8.9	5.70	0.3538	0.0893	0.3077	0.0892	−1.0311	6.73
1	−20.5	5.90	0.3388	0.149	0.2927	0.1489	−0.7869	6.69
0.5	−38.3	6.20	0.2989	0.2609	0.2528	0.2608	−0.4798	6.68
0.25	−52.7	6.44	0.2606	0.38	0.2145	0.3799	−0.2451	6.69
0.2	−52.7	6.44	0.2754	0.3364	0.2293	0.3363	−0.3270	6.77
0.1	−71.1	6.76	0.2109	0.5378	0.1648	0.5377	0.0202	6.74
0.05	−78.8	6.89	0.1891	0.6097	0.1430	0.6096	0.1364	6.75
Set II								
4	16.3	5.28	0.3592	0.0432	0.3131	0.0431	−1.3545	6.63
2	−6.8	5.67	0.345	0.0856	0.2989	0.0855	−1.0369	6.71
1	−23.3	5.95	0.3263	0.1502	0.2802	0.1501	−0.7644	6.71
0.5	−41.1	6.25	0.29	0.2647	0.2439	0.2646	−0.4580	6.71
0.25	−55.3	6.49	0.2691	0.4047	0.2230	0.4046	−0.2346	6.72
0.2	−54.7	6.48	0.2562	0.3631	0.2101	0.3630	−0.2559	6.73
0.1	−69.3	6.72	0.2073	0.5363	0.1612	0.5362	0.0286	6.70
0.05	−74.3	6.81	0.1908	0.5751	0.1447	0.5750	0.1059	6.70
acidic solution			**0.3791**	**0.0001**	**0.333**			
basic solution			**0.0461**	**1.0371**		**1.037**		
R_{PR}					**0.3211**			
100 W_1 = 30								
			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	log [PR$^-$]/[HPR][e]	pK_a[f]
Set I								
4	−19.7	5.79	0.3620	0.0741	0.3227	0.0703	−1.1532	6.94
2	−37.5	6.09	0.3455	0.1133	0.3062	0.1095	−0.9379	7.03
1	−55.8	6.40	0.3224	0.1894	0.2831	0.1856	−0.6747	7.07
0.5	−72.2	6.68	0.2767	0.3358	0.2374	0.3320	−0.3457	7.02
0.25	−81.1	6.83	0.2572	0.4078	0.2179	0.4040	−0.2232	7.05
0.2	−85.3	6.90	0.2558	0.4085	0.2165	0.4047	−0.2197	7.12
0.1	−90.3	6.98	0.2138	0.5411	0.1745	0.5373	−0.0029	6.98
0.05	−109.1	7.30	0.1686	0.6804	0.1293	0.6766	0.2274	7.07
Set II								
4	−21.1	5.81	0.3653	0.0646	0.3260	0.0608	−1.2206	7.03
2	−37.9	6.10	0.3475	0.1215	0.3082	0.1177	−0.9094	7.00
1	−56.6	6.41	0.3202	0.2021	0.2809	0.1983	−0.6426	7.05
0.5	−74.1	6.71	0.2765	0.3450	0.2372	0.3412	−0.3334	7.04
0.25	−86.7	6.92	0.2375	0.4668	0.1982	0.4630	−0.1229	7.04
0.2	−86.2	6.91	0.2449	0.4377	0.2056	0.4339	−0.1670	7.08
0.1	−97	7.09	0.2040	0.5664	0.1647	0.5626	0.0422	7.05
0.05	−107.2	7.27	0.1768	0.6643	0.1375	0.6605	0.1902	7.08
acidic solution			**0.3810**	**0.0038**	**0.3417**			
basic solution			**0.0393**	**1.0630**		**1.0592**		
R_{PR}					**0.3226**			
100 W_1 = 50								
			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	$\lambda_{\text{HPR}}^{\text{HPR}}$	$\lambda_{\text{PR}^-}^{\text{PR}^-}$	log [PR$^-$]/[HPR][e]	pK_a[f]
Set I								
4	−51.1	7.56	0.3592	0.0647	0.3189	0.0630	−1.1928	8.76
2	−67.2	7.84	0.3454	0.1155	0.3051	0.1138	−0.9168	8.75
1	−83.1	8.11	0.3187	0.1870	0.2784	0.1853	−0.6652	8.77
0.5	−94.6	8.30	0.2855	0.2921	0.2452	0.2904	−0.4150	8.72

Table 4 Continued

			100 $W_1 = 50$					
			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	log [PR⁻]/[HPR][e]	pK_a[f]
0.25	−116.7	8.67	0.2233	0.4863	0.1830	0.4846	−0.0655	8.74
0.2	−111.5	8.59	0.2462	0.4098	0.2059	0.4081	−0.1913	8.78
0.1	−129.3	8.89	0.1825	0.6030	0.1422	0.6013	0.1377	8.75
0.05	−132.2	8.94	0.1772	0.6242	0.1369	0.6225	0.1693	8.77
			Set II					
4	−50.3	7.55	0.3580	0.0637	0.3177	0.0620	−1.1981	8.75
2	−69.1	7.87	0.3373	0.1210	0.2970	0.1193	−0.8846	8.75
1	−84	8.12	0.3125	0.1951	0.2722	0.1934	−0.6369	8.76
0.5	−100.2	8.39	0.2693	0.3322	0.2290	0.3305	−0.3291	8.72
0.25	−109.2	8.55	0.2470	0.4166	0.2067	0.4149	−0.1859	8.73
0.2	−95.2	8.31	0.3221	0.2187	0.2818	0.2170	−0.6019	8.91
0.1	−122.8	8.78	0.2126	0.5317	0.1723	0.5300	−0.0005	8.78
0.05	−131.5	8.92	0.2090	0.5376	0.1687	0.5359	0.0135	8.91
acidic solution			**0.3769**	**0.0017**	**0.3366**			
basic solution			**0.0403**	**1.0382**		**1.0365**		
R_{PR}				**0.3247**				

[a] The buffers used were mixtures of KH_2PO_4/Na_2HPO_4. [b] emf is the electromotive force measured in mV for each solution. [c] Calculated from eq 3. [d] Corrected absorbance is calculated using eq 6. [e] Calculated using log eq 4. [f] Calculated using eq 2. [g] Each set represents individual replicate.

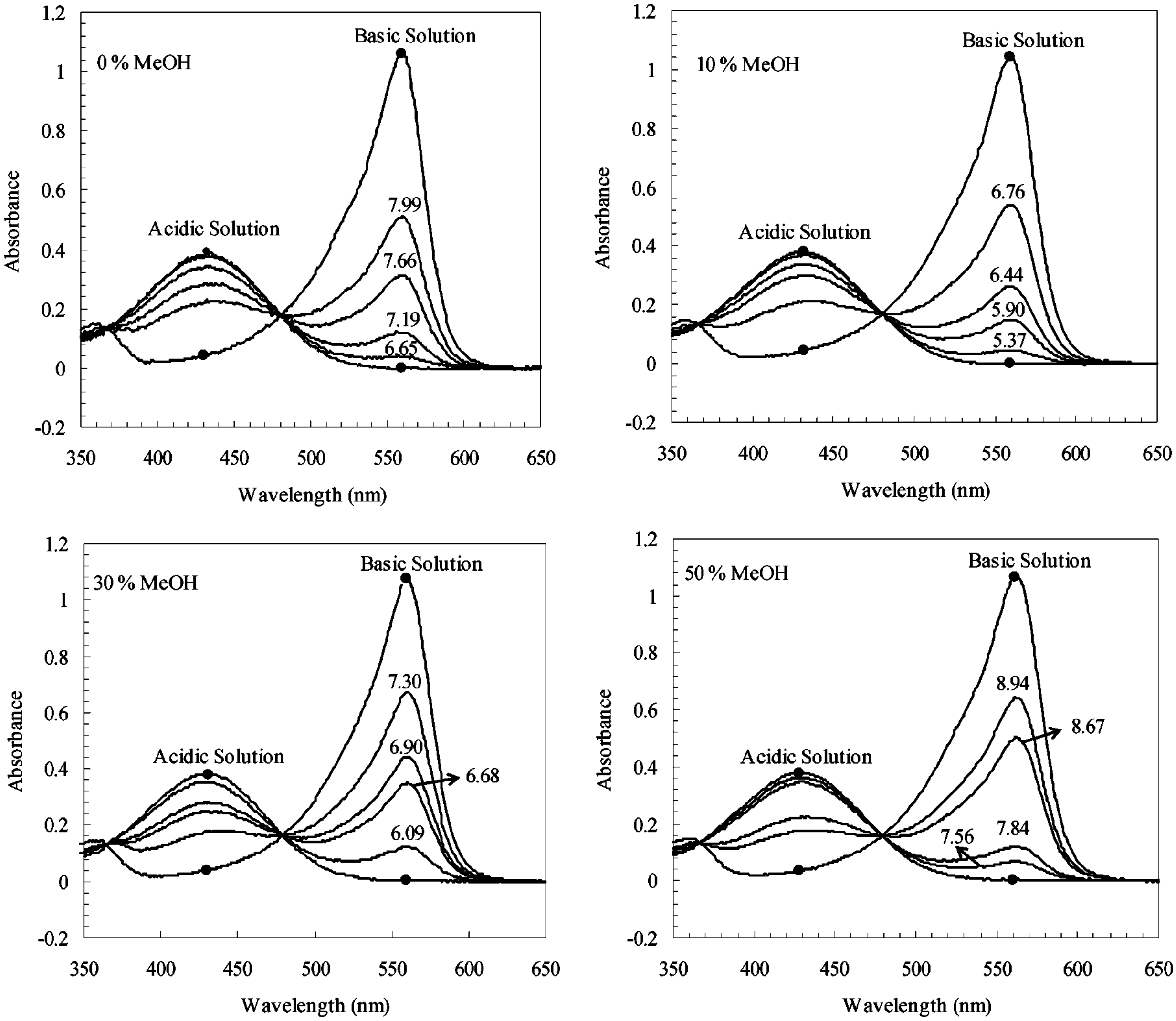


Figure 2. Absorption spectra of phenol red in methanol + water mixtures at $I = 2.5 \cdot 10^{-3}$ mol·dm^{-3} at different pH values (specified by the numbers above the absorption curves).

in cosolvent + water fractions. All cosolvent fractions were prepared by weight using N_2 purged distilled water. The concentrations of indicators in this work were $2.197 \cdot 10^{-5}$ mol·dm^{-3} for MR and $2.125 \cdot 10^{-5}$ mol·dm^{-3} for PR and fall within the range found in the literature.[13]

Procedure. The wavelengths at which HIn and In$^-$ (In = MR or PR) exhibited absorption maxima were determined in each cosolvent + water system and at every cosolvent concentration by investigating the absorbance versus wavelength relationship of two solutions: an acidic solution (0.1 mol·dm^{-3}

Table 5. Data for Phenol Red Indicator in Ethanol + Water at $T = 298.15$ K and Constant Ionic Strength ($I = 2.5 \cdot 10^{-3}$ mol·dm^{-3g})

$100\ W_1 = 10$

			measured absorbance		corrected absorbance[d]			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	log [PR$^-$]/[HPR][e]	pK_a[f]
Set I								
4	13.7	6.64	0.3681	0.0388	0.3268	0.0359	−1.4456	8.09
2	−4.5	6.95	0.3547	0.0759	0.3134	0.0730	−1.1191	8.07
1	−21.6	7.24	0.3409	0.1326	0.2996	0.1297	−0.8500	8.09
0.5	−38.9	7.53	0.3067	0.2326	0.2654	0.2297	−0.5491	8.08
0.25	−43	7.60	0.2995	0.2582	0.2582	0.2553	−0.4913	8.09
0.2	−29.6	7.38	0.3228	0.1868	0.2815	0.1839	−0.6713	8.05
0.1	−55.2	7.81	0.2732	0.3446	0.2319	0.3417	−0.3180	8.13
0.05	−65.6	7.99	0.2387	0.4478	0.1974	0.4449	−0.1335	8.12
Set II								
4	12.8	6.66	0.3700	0.0449	0.3287	0.0420	−1.3799	8.04
2	−4.9	6.96	0.3551	0.0785	0.3138	0.0756	−1.1045	8.06
1	−20.7	7.23	0.3384	0.1321	0.2971	0.1292	−0.8480	8.07
0.5	−37	7.50	0.3067	0.2246	0.2654	0.2217	−0.5645	8.07
0.25	−52.6	7.77	0.2727	0.3327	0.2314	0.3298	−0.3325	8.10
0.2	−40.4	7.56	0.2997	0.2361	0.2584	0.2332	−0.5309	8.09
0.1	−68.7	8.04	0.2241	0.4891	0.1828	0.4862	−0.0615	8.10
0.05	−71.6	8.09	0.2163	0.5123	0.1750	0.5094	−0.0224	8.11
acidic solution			**0.3788**	**0.0029**	**0.3375**			
basic solution			**0.0413**	**1.0372**		**1.0343**		
R_{PR}				**0.3263**				

$100\ W_1 = 30$

			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	log [PR$^-$]/[HPR][e]	pK_a[f]
Set I								
4	−19.5	7.03	0.3727	0.0476	0.3376	0.0433	−1.3685	8.40
2	−36.1	7.32	0.3564	0.0815	0.3213	0.0772	−1.0958	8.41
1	−52.2	7.59	0.3377	0.1339	0.3026	0.1296	−0.8448	8.43
0.5	−68.6	7.86	0.3055	0.2310	0.2704	0.2267	−0.5531	8.42
0.25	−80.4	8.06	0.2769	0.3161	0.2418	0.3118	−0.3661	8.43
0.1	−95.1	8.31	0.2385	0.4437	0.2034	0.4394	−0.1420	8.45
0.05	−100.2	8.40	0.2238	0.4958	0.1887	0.4915	−0.0608	8.46
Set II								
4	−20.5	7.05	0.3695	0.0406	0.3344	0.0363	−1.4409	8.49
2	−36.5	7.32	0.3581	0.0842	0.3230	0.0799	−1.0832	8.40
1	−50.7	7.56	0.3404	0.1302	0.3053	0.1259	−0.8612	8.42
0.5	−69	7.87	0.3126	0.2411	0.2775	0.2368	−0.5454	8.42
0.25	−81.8	8.09	0.2719	0.3262	0.2368	0.3219	−0.3432	8.43
0.1	−94	8.29	0.2444	0.4297	0.2093	0.4254	−0.1685	8.46
0.05	−101.6	8.42	0.2147	0.5317	0.1796	0.5274	−0.0087	8.43
acidic solution			**0.3822**	**0.0043**	**0.3471**			
basic solution			**0.0351**	**1.0442**		**1.0399**		
R_{PR}				**0.3338**				

$100\ W_1 = 50$

			measured absorbance		corrected absorbance			
ratios of buffer solutions[a]	emf[b]	pH[c]	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	$\lambda_{\mathrm{HPR}}^{\mathrm{HPR}}$	$\lambda_{\mathrm{PR}^-}^{\mathrm{PR}^-}$	log [PR$^-$]/[HPR][e]	pK_a[f]
Set I								
4	−42.5	6.95	0.3674	0.0324	0.3273	0.0322	−1.4881	8.44
2	−64.5	7.32	0.3566	0.0668	0.3165	0.0666	−1.1579	8.48
1	−79.8	7.58	0.3462	0.1139	0.3061	0.1137	−0.9111	8.49
0.5	−90.7	7.77	0.3240	0.1732	0.2839	0.1730	−0.6961	8.46
0.25	−108.8	8.07	0.2930	0.2940	0.2529	0.2938	−0.4159	8.49
0.1	−102	7.96	0.2966	0.2465	0.2565	0.2463	−0.4986	8.46
0.05	−122.6	8.31	0.2979	0.2480	0.2578	0.2478	−0.4982	8.80
Set II								
4	−46	7.01	0.3673	0.0408	0.3272	0.0406	−1.3873	8.40
2	−63	7.30	0.3584	0.0680	0.3183	0.0678	−1.1526	8.45
1	−80.2	7.59	0.3437	0.1181	0.3036	0.1179	−0.8918	8.48
0.5	−93.7	7.82	0.3162	0.1956	0.2761	0.1954	−0.6312	8.45
0.25	−108.1	8.06	0.2870	0.2751	0.2469	0.2749	−0.4344	8.50
0.1	−121.3	8.28	0.2444	0.3851	0.2043	0.3849	−0.2059	8.49
0.05	−123.9	8.33	0.2546	0.3935	0.2145	0.3933	−0.2177	8.55
acidic solution			**0.3767**	**0.0002**	**0.3366**			
basic solution			**0.0401**	**1.0191**		**1.0189**		
R_{PR}				**0.3303**				

[a] The buffers used were mixtures of KH_2PO_4/Na_2HPO_4. [b] emf is the electromotive force measured in mV for each solution. [c] Calculated from eq 3. [d] Corrected absorbance is calculated using eq 6. [e] Calculated using log eq 4. [f] Calculated using eq 2. [g] Each set represents individual replicate.

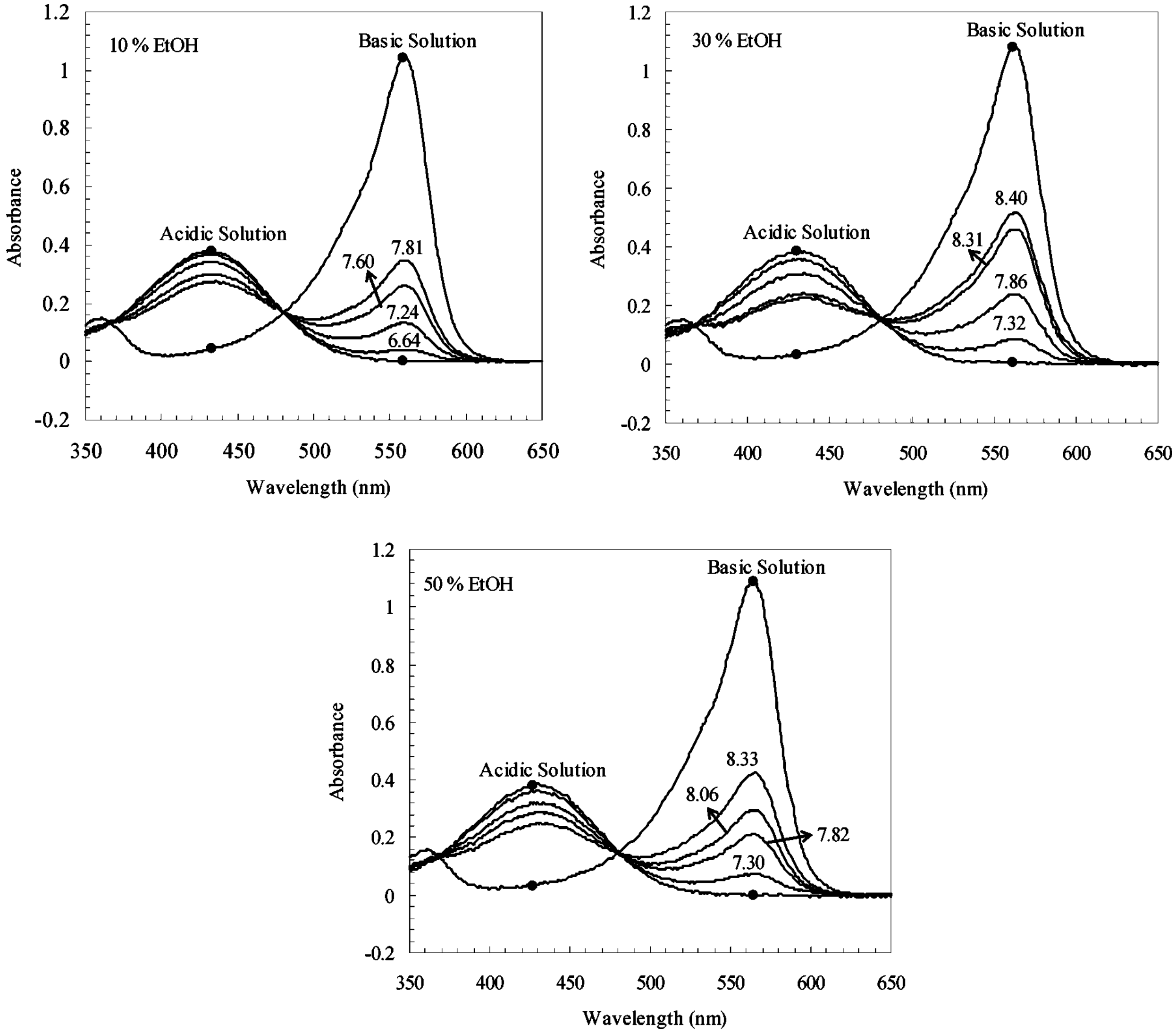


Figure 3. Absorption spectra of methyl red in ethanol + water mixtures at $I = 2.5 \cdot 10^{-3}$ mol·dm^{-3} at different pH values (specified by the numbers above the absorption curves).

HCl and $2.5 \cdot 10^{-3}$ mol·dm^{-3} KH_2PO_4 for MR and PR, respectively) which contained the indicator entirely in the form HIn and a basic solution (0.04 mol·dm^{-3} NaOAc and 0.1 mol·dm^{-3} NaOH for MR and PR, respectively) which contained the indicator entirely in the form In^-.[24] Absorption maxima, λ_{HIn} and λ_{In^-}, were recorded at every wt % cosolvent, 100 W_1.

The relative amounts of the acid and base forms of each indicator as a function of pH were measured in series of solutions of constant low total ionic strength ($I = 2.5 \cdot 10^{-3}$ mol·dm^{-3}), constant total amount of indicator ($2.197 \cdot 10^{-5}$ mol·dm^{-3} for MR and $2.125 \cdot 10^{-5}$ mol·dm^{-3} for PR), and varying amounts of buffer solutions (HOAc:NaOAc and KH_2PO_4:Na_2HPO_4 for MR and PR, respectively) in binary cosolvent + water solvents.[25] At this low ionic strength, it is hypothesized that ion–ion interactions are minimal and that the net effects of cosolvents on the dissociation of MR and PR indicators are driven primarily by solvent−solvent and solvent–ion interactions. For example, to measure the relative amount of the acid and base form of the PR indicator in 20 wt % ethanol, a series of solutions containing (0, 0.05, 0.1, 0.2, 0.25, 0.5, 2, and 4) KH_2PO_4:Na_2HPO_4 were prepared by adding a constant amount of PR stock solution to varying portions of standard KH_2PO_4 ($2.5 \cdot 10^{-3}$ mol·dm^{-3}) and Na_2HPO_4 ($2.3 \cdot 10^{-3}$ mol·dm^{-3}) solutions (prepared each in 20 wt % ethanol). A Cary 50 UV–vis spectrophotometer (Varian Instruments, Walnut Creek, Ca) equipped with a dip probe was used to measure absorbance. In each wt % cosolvent, baseline corrections were done by measuring the absorbance of a blank solution containing the solvent of interest (e.g., 10 wt % methanol) and subtracting it from the absorbance of the samples at λ_{HIn} and λ_{In^-}.[26]

In each solution and at each wt % cosolvent, emf was measured in millivolts using an Accumet pH meter equipped with a Sure-Flow glass combination electrode (Orion) preconditioned in a solution that contained the wt % cosolvent of interest for at least 10 days to reduce electrical potential drifts.[9] The primary reference standard selected for this study to calibrate the pH electrode was a solution of 0.05 mol·kg^{-1} of potassium hydrogen phthalate prepared in each cosolvent + water fraction. The pH_{PS} values of 0.05 mol·kg^{-1} of potassium hydrogen phthalate at T = 298.15 K were taken from the literature[27] and are summarized in Table 1. The time needed for readings to stabilize varied from (5 to 20) min.

All measurements were conducted at $T = (298.15 \pm 2.0)$ K. The temperature variation was somewhat large (± 2.0 K) and presented the range of temperatures recorded for all the studied solutions in the various wt % cosolvents during the overall period of study (one month). However, this variation was not of concern because the effect of temperature on the dissociation

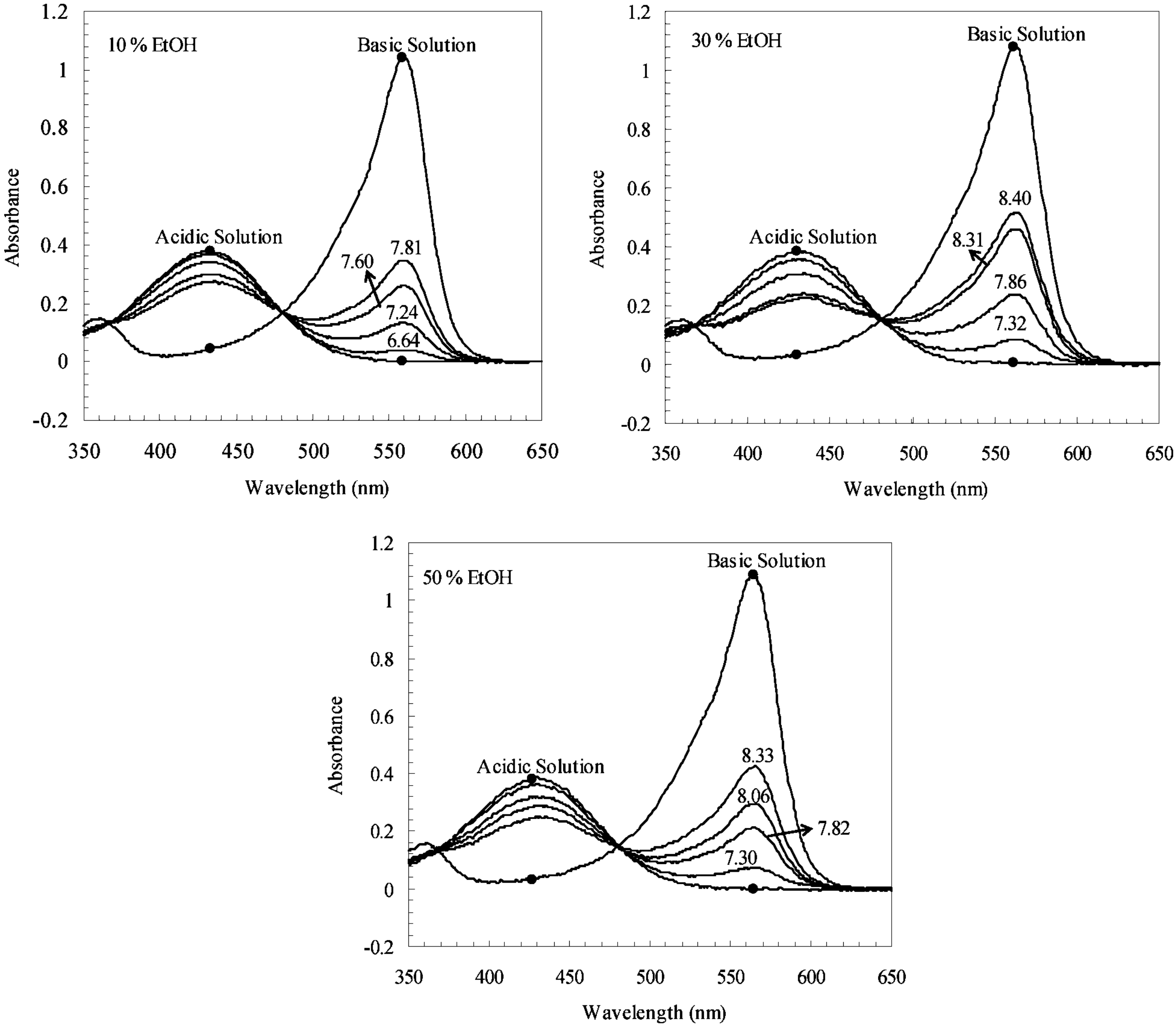


Figure 4. Absorption spectra of phenol red in ethanol + water mixtures at $I = 2.5 \cdot 10^{-3}$ mol·dm^{-3} at different pH values (specified by the numbers above the absorption curves).

constants of MR and PR is relatively small.[13,14,24] For instance, the pK_a value of MR in aqueous solutions was 5.05 ± 0.05 in the range T = (298.15 to 303.15) K.[24] For PR in seawater (35 % salinity), these pK_a's were 7.495 ± 0.006 and 7.451 ± 0.006 at T = (298.25 and 303.45) K, respectively.[14] These differences, which are only apparent at the second decimal place and fall within the uncertainties measured for each constant, can be for the purpose of this study considered negligible. The experimental values obtained for MR and PR indicators (emf and absorbance) along with calculated values of pH, log [In$^-$]/[HIn], and pK_a in (0, 10, 30, and 50) wt % in methanol–water and ethanol–water mixtures at T = 298.15 K and $I = 2.5 \cdot 10^{-3}$ mol·dm^{-1} are presented in Tables 2 to 5. Each series represents a separate replicate.

Results and Discussion

The electronic absorption spectra of MR and PR in binary aqueous methanol and ethanol at various pH values at (350 to 650) nm intervals are shown in Figures 1 to 4. In water solutions, the absorption maxima of the acid and basic forms of MR and PR were at λ_{HMR} = 520 nm and λ_{MR^-} = 425 nm and λ_{HPR} = 433 nm and λ_{PR^-} = 558 nm, respectively. These values agree well with published ones.[13,25] There was no change in the wavelength at which the absorption maxima of the acidic and basic solution occurred in the studied cosolvent + water systems (Figures 1 to 4). However, slight changes in the peak width among cosolvents were observed. This change in peak width may be attributed to the presence of several species of the indicator (potential isomers) molecule.[10]

The variations in the acid dissociation constants for MR and PR indicators with wt % methanol and ethanol are shown in Figure 5. The obtained values of pK_a of MR (5.07 ± 0.09) and PR (8.05 ± 0.03) in water are in good agreement with values reported in the literature.[13,14,24,25,28] In methanol + water and for both indicators, pK_a values decreased from water to 10 wt % methanol and slightly increased from (10 to 30) wt % methanol but remained lower than their values in water. At 50 wt % methanol, pK_a values of MR and PR were larger than that of water (Figure 5a). In ethanol + water, pK_a slightly increased (i.e., acid dissociation constant, K_a, decreased) as wt % cosolvent increased (Figure 5b). This increase in the pK_a of both indicators in (10 to 50) wt % ethanol and 50 wt % methanol can be interpreted in terms of the variations in the electrostatic effects resulting from the change in the dielectric constant of the medium, upon the addition of organic solvent. To illustrate, consider the acid dissociation constant of an indicator, In, in a pure aqueous medium, $K_{a(w)}$. This latter constant is related to

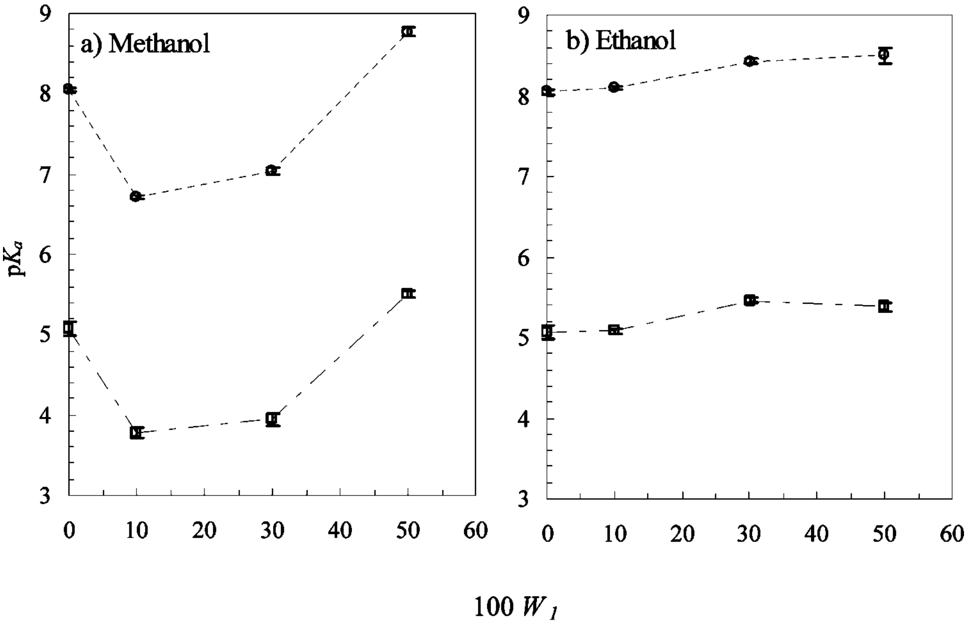


Figure 5. Variation of the acidity constant values, pK_a, of ○, PR and □, MR with wt % methanol and ethanol at $T = 298.15$ K and $I = 2.5 \cdot 10^{-3}$ mol·dm^{-3}. Error bars represent the standard deviation in the values of pK_a.

the acid dissociation constant, K_a, of In in mixed aqueous–organic solvent, by the following equation:[29]

$$K_{a(w)} = K_a\left(\frac{\gamma_{\text{In}^-}\gamma_{\text{H}^+}}{\gamma_{\text{HIn}}}\right) \tag{7}$$

where γ is the activity coefficient of the respective species in a mixed aqueous–organic medium relative to that in pure water. Water is a solvent of high solvating ability (i.e., donor number, DN = 33)[31] and high dielectric constant ($\epsilon = 87.3$), and therefore, it is able to dissociate the acid and stabilize the produced anion and hydrogen ion. If the interactions between the indicator and the solvents are governed primarily by electrostatic forces, then the addition of methanol (DN = 19, $\epsilon = 32.6$) and ethanol (DN = 15, $\epsilon = 24.3$) with lower donor numbers and dielectric constants relative to water would decrease the extent of interaction between the acid anion and proton with the solvent and according to eq 7 would trigger a decrease in their acidity constants (i.e., increase in pK_a). The fact that the pK_a of MR and PR increased in methanol + water (only after 10 %) and in ethanol + water ($0 < 100\ W_1 < 50$) (Figure 5) indicates that these constants are governed primarily by electrostatic effects[20–22,30] dictated by the solvent properties, namely, its solvating ability (as expressed by the Gutmann donor number)[29] and dielectric constant.[20] No explanation for the decrease in the acidity constant of both indicators from water to 10 wt % methanol is currently available. Specific solvent−solvent and solvent–ion interactions, the nature of which could not be elucidated from this particular study, might be involved.

Conclusions

The acid dissociation constants of methyl red and phenol red acid–base indicators were determined in methanol–water and ethanol–water cosolvents at $T = 298.15$ K and at a constant ionic strength of $I = 2.5 \cdot 10^{-3}$ mol·dm^{-1} using a spectrophotometric method. In ethanol + water, the calculated pK_a values of MR and PR increased with wt % [(0 to 50) %] cosolvent. In methanol + water, pK_a of both indicators increased only after 10 wt % methanol. This indicates that for both cosolvents and at the range of concentrations used the acid dissociation constants of MR and PR are primarily governed by electrostatic factors.

Appendix

Symbols

A	Absorbance
C_T	Total concentration
DN	Donor number
emf	Electromotive force
F	Faraday constant
I	Ionic strength
K_a	Acid dissociation constant
pK_a	Negative log acid dissociation constant
R	Universal gas constant
T	Absolute temperature
W_i	Cosolvent fraction

Greek

ϵ	Dielectric constant of the medium
γ	Activity coefficient
λ	Wavelength

Subscripts

HIn	Acid form of an indicator
HMR	Methyl red (acid form)
HPR	Phenol red (acid form)
In$^-$	Basic form of an indicator
MR$^-$	Methyl red (basic form)
PR$^-$	Phenol red (basic form)
PS	Primary standard

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