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THERMODYNAMIC PARAMETERS OF SOME SCHIFF BASES DERIVED FROM 5,7-DIHYDROXY-6-FORMYL-2-METHYLBENZOPYRAN-4-ONE

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Abstract

Potentiometric studies on Schiff bases derived from 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one were carried out at different ionic strengths (0.02, 0.04, 0.06, 0.10 and 0.14 M NaCl), at different temperatures (25, 35, 45 and 55°C) and in ethanol-water media of varying compositions (60, 70, 80 and 90% v/v). The ionization constants of the Schiff bases were investigated in the presence of different organic solvents (70% v/v), e.g. methanol, ethanol, *n*-propanol, isopropanol, acetone, DMSO and DMF-water media. The thermodynamic parameters (ΔG, ΔH and ΔS) were also calculated.

Keywords: benzopyran-4-one, chromone, ionic strength, potentiometry, Schiff bases, temperature and solvent

Introduction

Many authors [1–3] have determined the ionization constants of a large number of Schiff bases. The effects of the solvent and the substituents on the protonation constants of sixteen Schiff bases derived from salicylaldehyde and substituted anilines were earlier studied under nitrogen atmosphere and at different percentages of dioxane in dioxane-water media [4].

The present investigation deals with a potentiometric study to evaluate the proton-ligand ionization constants of some Schiff bases derived from the reactions of 5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one with some aromatic amines such as aniline, anthranilic acid, *o*-aminophenol, 5-chloro-2-aminophenol and 4-amino-3-hydroxybenzenesulphonic acid. The effects of ionic strength, temperature and solvent on the ionization of the investigated Schiff bases were studied. The thermodynamic parameters (ΔG, ΔH and ΔS) of the ionization process were also determined. The studies were carried out by using the Calvin-Bjerrum [5, 6] pH-metric titration technique as adopted by Irving and Rossotti [7].

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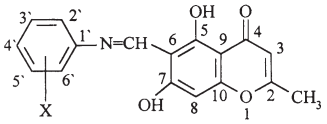
Experimental

All chemicals and reagents used in the present study were either of A. R. grade or purified by recommended methods [8], and H_2O was distilled twice. The Schiff bases were prepared by the condensation of equimolar amounts (0.01 mol) of chromone and amine for at least 1 h in ethanol [9] for all amines except 4-amino-3-hydroxybenzenesulphonic acid, which was dissolved in 4% (w/w) NaOH–H_2O mixture because of its insolubility in ethanol. The Schiff bases obtained were recrystallized from toluene (Schiff base I), DMF (Schiff bases II and V) or ethanol (Schiff bases III and IV) and then subjected to elemental analysis for C, H, N, Cl and S content, and to mass spectroscopy, IR spectroscopy, ^{1}H-NMR spectroscopy and UV spectroscopy; the results were quite satisfactory. The resulting Schiff bases I–V have the following general structure:



The derivatives used were

(I) *X*=H [N-phenyl-5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one anil]
(II) *X*=2’-COOH [N-(2-carboxyphenyl)-5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one anil]
(III) *X*=2’-OH [N-(2-hydroxyphenyl)-5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one anil]
(IV) *X*=2’-OH, 5’-Cl [N-(5-chloro-2-hydroxyphenyl)-5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one anil]
(V) *X*=2’-OH, 4’-SO_3H [N-(2-hydroxybenzene-4-sulphonic acid)-5,7-dihydroxy-6-formyl-2-methylbenzopyran-4-one anil]

The potentiometric titrations were carried out as recommended and described previously [5–7]. Measurements were made in 70% (v/v) ethanol-water medium at an ionic strength of 0.14, 0.10, 0.06 or 0.02 M NaCl, at 25°C, in order to study the effect of ionic strength, and at 55, 45, 35 or 25°C and 0.10 M NaCl, in order to study the effect of temperature. Measurements were also carried out at 0.10 M NaCl and 25°C in 60, 70, 80 or 90% (v/v) ethanol-water media in order to investigate the effect of solvent composition variation, and in 70% (v/v) methanol, ethanol, *n*-propanol, *iso*-propanol, acetone or DMSO-water media in order to study the effects of different solvents.

Results and discussion

From the potentiometric titration studies, the $\bar{n}_A$ values (the average number of replaceable hydrogens bound to the ligand) were calculated at various pH values, using previously described methods [1–3]. Representative formation curves relating pH to the corresponding $\bar{n}_A$ values were plotted (Fig. 1). The results show that all the OH protons are titrable, giving two ionization steps for Schiff base I, three ionization steps for Schiff bases II, III and IV, and four ionization steps for Schiff base V (Table 1).

Table 1 Proton-ligand formation constants of Schiff bases I–V at different ionic strengths and temperatures

Schiff base		pK_1	pK_2	pK_3	pK*	T/°C (K)	pK_1	pK_2	pK_3	pK*
I	0.14	6.61	8.26	–	–	55	6.21	7.25	–	–
II		7.15	9.78	–	6.02	(328)	6.43	7.81	–	5.56
III		6.51	8.19	10.98	–		6.00	7.15	10.12	–
IV		6.99	8.90	11.20	–		6.36	7.49	10.22	–
V		5.01	7.80	10.26	3.40		4.62	7.06	9.85	3.20
I	0.10	6.86	8.41	–	–	45	6.34	7.66	–	–
II		7.30	9.44	–	6.41	(318)	6.73	8.39	–	5.89
III		6.70	8.26	11.22	–		6.62	7.53	10.45	–
IV		7.22	9.17	11.47	–		6.61	8.10	10.57	–
V		5.47	8.11	10.26	3.54		4.99	7.38	10.26	3.36
I	0.06	7.10	8.80	–	–	35	6.62	8.02	–	–
II		7.55	10.20		6.53	(308)	7.02	9.21	–	6.19
III		7.07	8.66	11.35	–		6.47	7.91	10.82	–
IV		7.33	10.01	11.44	–		6.95	8.81	10.97	–
V		6.10	8.33	10.89	3.98		5.14	7.73	10.62	3.42
I	0.02	7.35	8.90	–	–	25	6.86	8.41	–	–
II		7.73	10.42		6.72	(298)	7.30	9.44	–	6.42
III		7.24	9.73	11.45	–		6.70	8.26	11.22	–
IV		7.69	10.35	11.65	–		7.22	9.17	11.47	–
V		7.20	8.69	11.05	4.20		5.47	8.11	10.62	3.54
I*	0.00	7.47	9.55			0	7.40	9.37	–	–
II*		7.83	10.5		6.78	(273)	8.03	11.25	7.17	7.17
III*		7.39	9.71	11.56			7.25	9.19	12.10	–
IV*		7.75	10.65	11.70			7.82	10.92	12.29	–
V*		7.39	8.81	11.23	4.35		5.89	8.62	12.03	3.75

pK_1=pK_{OH} for OH at position 7, pK_2=pK_{OH} for OH at position 5, pK_3=pK_{OH} phenolic and pK*=pK_{COOH} (II) and pK_{SO_3H} (V). These are the mean pK_a values of the values obtained by interpolation for half $\bar{n}_A$ values and log term methods

*Values obtained from linear regression equation.

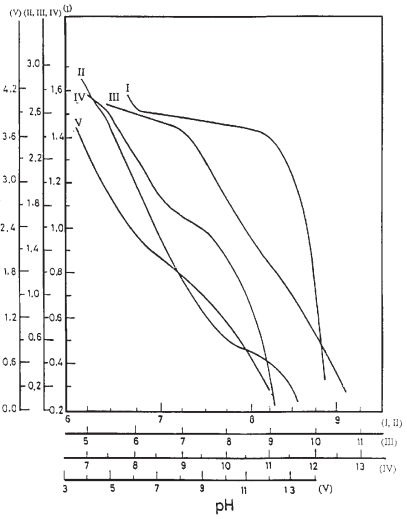


Fig. 1 Representative proton-ligand formation curves for Schiff bases I–V at 0.1 M NaCl, 25°C and 70% v/v ethanol-water medium

Effects of substitution on the ionization constants

For the chromone moiety, both the OH at position 5 and the OH at position 7 were assumed to be involved in hydrogen-bonding, with the C=O in position 4 [10] and the N atom of the azomethine group [1], respectively. This assumption was confirmed by the shifts in their IR bands to longer wavelength (the OH band is observed as a broad band at 3700–3500 cm^{-1}, while the C=O band is shifted to 1651 cm^{-1} and the C=N band to 1625 cm^{-1}). Since the electronegativity of the O atom (3.5) is higher than that of N (3.1), the hydrogen-bonding with O is stronger than that with N, and the OH proton at position 7 will ionize at lower pH than that for the OH proton at position 5, thereby decreasing the value of pK_{OH} of the OH at position 7 relative to that of the OH at position 5. The carboxylate group in Schiff base II displays a higher than expected pK value [6.42 at 70% (v/v) ethanol-water, 25°C and 0.1 M NaCl]. This can be attributed to its hydrogen-bonding with the N atom of the azomethine group [1]. From the results obtained, the pK_a values of the investigated Schiff bases follow the sequence II>IV>I>III>V. This can be illustrated as follows:

1. For the *o*-carboxy derivative II, the ionization of the carboxylic group (pK_a = 6.42) results in the electron-donating carboxylate ion, which increases the electron density around the N atom of the azomethine group, increasing its hydrogen-bonding with the OH at position 7, so the net result is to increase the value of pK_{OH} in the case of Schiff base II more than that of I.

2. For Schiff base IV, the presence of the Cl atom with its positive mesomeric effect increases the electron density around the N atom of the azomethine group. This

will increase the hydrogen-bonding of the OH group at position 7, decreasing its ionization and increasing its pK_a value.

3. For Schiff base III, the OH group on the phenyl moiety will be involved in hydrogen-bonding with the azomethine group. Such additional hydrogen-bonding may lead to a lower pK_{OH} value for the OH group at position 7 since the phenolic H at position 7 will be less strongly held by the azomethine N.

4. For derivative V, the $-I$ effect of the SO_3H group decreases the electron density on the phenyl moiety, and consequently that on the N atom of the azomethine group, resulting in a decrease in hydrogen-bonding with the OH group at position 7, thereby facilitating the release of the OH proton at position 7 and decreasing its pK_a value.

Effect of ionic strength

The ionic strength of the medium (μ) is given by the relation [11]

$$\mu=\frac{1}{2}\Sigma Z_i^2 m_i \qquad (1)$$

where m_i are the molar concentrations of the ions and Z_i are their charges. This is related to the activity coefficients of the ions in solution by the following relation:

$$\log_{10}\gamma_{\pm}=-\alpha Z_+|Z_-|\mu^{1/2} \qquad (2)$$

where $\gamma_{\pm}$ is the activity coefficient of cations and anions, α is the degree of dissociation, and $Z_+|Z_-|$ is the positive product of the ionic charges. When the concentration of free ions in the solution is very low, $\gamma_{\pm}$ becomes close to unity and the ions are not affected by each other. At higher concentrations, $\gamma_{\pm}$ is not close to unity and the ions of opposite charges attract each other [12]. Hence, H^+ is attracted to Cl^- in the solution, increasing the ionization process and decreasing the pK_a values of the Schiff bases with increase of the ionic strength of the solution (Table 1). This discussion is in agreement with the Debye-Hückel equation [5]:

$$pK_a=pK^o-[A\sqrt{\mu}/(1+\alpha)\sqrt{\mu}]+C_{\mu} \qquad (3)$$

where pK_a is the ionization constant at a given ionic strength, pK^o is the thermodynamic ionization constant at zero ionic strength, A and α are constants, and μ is the ionic strength of the medium.

The plot of $\sqrt{\mu}$ *vs.* pK_a (Fig. 2) gives a linear relation [13] with correlation coefficient >0.97. The pK_a value at μ=zero is obtained by applying the linear regression equation.

Effect of temperature [14]

The ionization constants were calculated at various temperatures (25, 35, 45 or 55°C) in 70% (v/v) ethanol-water medium and 0.1 M NaCl. The pK_a values at 0°C were obtained by applying a linear regression equation. The values given in Table 1 indicate

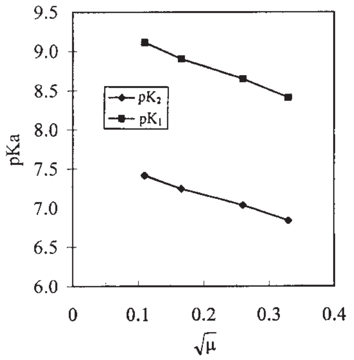


Fig. 2 Representative plots of pK_a values of Schiff base I *vs.* $\sqrt{\mu}$ at 25°C in 70% v/v ethanol-water medium

that the processes of dissociation of the Schiff bases are temperature-dependent and the acidity constants increase linearly with increasing temperature (the temperature coefficient (the rate of change in pK_a with temperature) ranging from 0.01 to 0.04). This can be attributed to the increase in thermal energy, and hence in the activity of the ions and molecules in solution; in other words, an increase of temperature results in a breakdown of the hydrogen-bonding and a faster increase in the ionization process. The values of the free energy change ΔG for the ionization process are calculated from the equation

$$\Delta G = -2.303RT \log K = 2.303RT\,\mathrm{p}K_a \quad (4)$$

The enthalpy change ΔH and entropy change ΔS are related to ΔG by the equation:

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

$$2.303RT\,\mathrm{p}K_a = \Delta H - T\Delta S \quad (6)$$

$$\mathrm{p}K_a = \Delta H/2.303R\cdot 1/T - \Delta S/2.303R \quad (7)$$

The plot of pK_a *vs.* $1/T$ is a straight line (with variation coefficient ≥0.97; its slope is $\Delta H/2.303R$ and its intercept is $\Delta S/2.303R$ (Fig. 3). The values of the thermodynamic parameters of the ionization processes (listed in Table 2) indicate that the dissociation processes are temperature-dependent and the acidity constants increase with elevation of temperature. The thermodynamic parameters of the processes of dissociation of the investigated Schiff bases reveal that [15]:

1. The positive values of ΔH indicate that the dissociation processes are accompanied by the absorption of heat and the processes are endothermic.

2. The negative values for ΔS may be due to the increased order produced by solvation, i.e. the sum of the bound water molecules is more than the water molecules originally accompanying the undissociated Schiff base molecules.

3. The large positive values of ΔG indicate that the processes of dissociation of the investigated Schiff bases are not spontaneous.

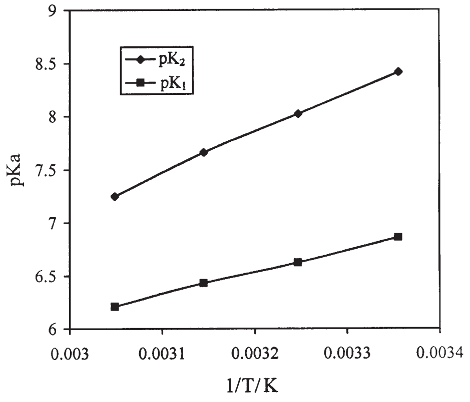


Fig. 3 Representative plots of pK_a values of Schiff base I *vs.* 1/T at 0.1 M NaCl in 70% v/v ethanol-water medium

Effect of solvent

The effect of the solvent on the ionization process can be attributed to the decrease in hydrogen-bonding in water by the organic solvent, the dielectric constant of the mixed solvent and the protonation of the organic solvent molecules [16]. The effects of the solvent on the ionization of the investigated Schiff bases were studied at 25°C and 0.1 M NaCl in various ethanol-water media (60, 70, 80 or 90% (v/v) and in 70% v/v methanol, ethanol, *n*-propanol, isopropanol, acetone and DMSO-water media.

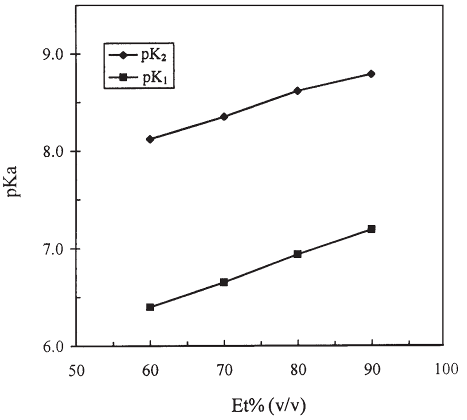


Fig. 4 Representative plots of pK_a values of Schiff base I *vs.* percentage of ethanol at 0.1 M NaCl and 25°C

Table 2 Thermodynamic parameters of the ionization constants of Schiff bases I–V

Schiff base	pK	Mean pK_a value	Temp. T/K	ΔG/ kJ mol^{-1}	ΔH/ kJ mol^{-1} K^{-1}	ΔS/ J mol^{-1} K^{-1}
I	pK_1	6.21	328	38.308	31.897	113.87
		6.34	318	38.538		
		6.62	308	38.975		
		6.86	298	39.076		
	pK_2	7.25	328	45.455	42.477	150.23
		7.66	318	46.562		
		8.02	308	47.217		
		8.41	298	47.905		
II	pK*	5.56	328	34.859	63.717	108.955
		5.89	318	35.802		
		6.19	308	36.443		
		6.42	298	36.570		
	pK_1	6.43	328	40.314	38.230	123.291
		6.73	318	40.908		
		7.02	308	41.329		
		7.30	298	41.582		
	pK_2	7.81	328	48.966	33.037	131.191
		8.39	318	50.999		
		9.21	308	53.195		
		9.44	298	53.773		
III	pK_1	6.00	328	37.618	33.036	117.557
		6.36	318	38.052		
		6.42	308	38.091		
		6.70	298	39.165		
	pK_2	7.15	328	44.882	32.806	141.812
		7.53	318	45.771		
		7.91	308	46.569		
		8.26	298	47.051		
	pK_3	10.12	328	63.449	68.749	191.571
		10.45	318	63.520		
		10.82	308	63.702		
		11.22	298	63.912		

Table 2 Continued

Schiff base	pK	Mean pK_a value	Temp. T/K	ΔG/ kJ mol^{-1}	ΔH/ kJ mol^{-1} K^{-1}	ΔS/ J mol^{-1} K^{-1}
IV	pK_1	6.26	328	39.875	47.787	115.784
		6.61	318	40.179		
		6.95	308	40.917		
		7.22	298	41.127		
	pK_2	7.39	328	46.960	106.194	169.945
		8.10	318	49.236		
		8.81	308	51.868		
		9.17	298	52.235		
	pK_3	10.22	328	64.076	57.414	183.724
		10.57	318	64.250		
		10.97	308	64.584		
		11.47	298	65.336		
V	pK*	3.20	328	20.063	33.732	60.284
		3.36	318	20.424		
		3.42	308	20.788		
		3.70	298	21.076		
	pK_1	4.62	328	28.966	52.131	93.967
		4.99	318	29.378		
		5.14	308	30.261		
		5.47	298	31.158		
	pK_2	7.06	328	44.264	63.717	156.166
		7.35	318	44.677		
		7.73	308	45.510		
		8.11	298	64.197		
	pK_3	9.85	329	61.756	58.406	165.543
		10.26	318	62.366		
		10.62	308	62.524		
		11.04	298	62.886		

pK_1=pK_{OH} for OH at position 7, pK_2=pK_{OH} for OH at position 5, pK_3=pK_{OH} phenolic, pK*=pK_{COOH} (II), pK_{COOH} and pK_{SO_3H} (V)

For different percentages of ethanol

The results listed in Table 3 show that the ionization process decreases with increasing ethanol content (Fig. 4), in consequence of the decrease in hydrogen-bonding between water and the ionized protons, which assists the ionization process [17]. The pK_a values in pure H_2O and pure ethanol (i.e. 0 and 100% EtOH) were obtained by applying a linear regression equation.

For different solvents

For different solvents, the ionization process is affected by both the dielectric constants of the solvents [17] and the extent of hydrogen-bonding to the organic solvent [18]. The relation relating the ionization constant to the dielectric constant of the medium is

$$\mathrm{p}K_a = \mathrm{p}K_o + \frac{0.43}{RT}\frac{Z_1 Z_2}{r_1 r_2}\frac{1}{D} \tag{8}$$

where pK_a and pK_o are the dissociation constants in the solvent mixture and pure water, respectively, Z_1 and Z_2 are the charges carried by the ions at equilibrium, r_1 and r_2 are the radii of the ions, and D is the dielectric constant of the solvent. From the above equation, it is evident that, if the dielectric constant of the solvent is the predominant factor affecting the change in pK_a with solvent, the relationship pK_a *vs.* $1/D$ must be linear. However, the data obtained (listed in Table 3) show that the dielectric constant is not the predominant factor, the sequence of increasing pK_a values being methanol<ethanol<1-propanol<2-propanol<acetone<DMSO; acetone has a higher dielectric constant than those of 1- or 2-propanol (as indicated by Table 3), but it gives higher pK_a values; this can be illustrated in that the extents of hydrogen-bonding in the 1- or 2-propanol-water media are higher than that in acetone-water medium, so that the pK_a values in acetone are higher than those in 1- or 2-propanol [19].

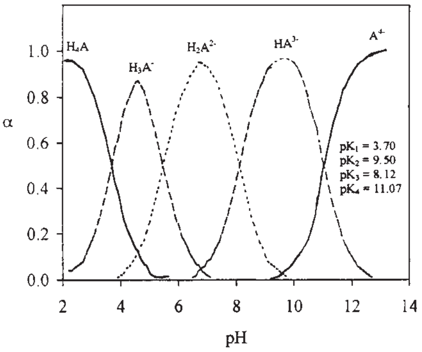


Fig. 5 Distribution curves of the different species of Schiff base V at 0.1 M NaCl, 25°C in 70% v/v ethanol-water medium

Distribution of different species of Schiff bases during titration

The degrees of distribution of the different species in solution were calculated by using the Hinderson equation:

Table 3 Proton-ligand formation constants of Schiff bases I–V in different ethanol-water media and solvents

Schiff base	Et/%	pK_1	pK_2	pK_3	pK*	Solvent 70%	pK_1	pK_2	pK_3	pK*
I	60	6.40	8.12	–	–	MeOH	6.77	8.26	–	–
II		7.00	9.33	–	6.01		7.13	9.23		6.32
III		6.29	7.89	10.97	–		6.46	8.04	11.00	–
IV		6.87	9.80	11.11	–		7.00	9.04	11.18	–
V		5.17	7.72	10.82	3.17		5.31	7.91	10.84	3.41
I	70	6.86	8.41	–	–	EtOH	6.85	8.41	–	–
II		7.30	9.44	–	6.42		7.30	9.44		6.42
III		6.70	8.26	11.22	–		6.70	8.26	11.22	–
IV		7.22	9.17	11.47	–		7.22	9.17	11.47	–
V		5.47	8.11	11.04	3.50		5.47	8.11	11.04	3.50
I	80	6.94	8.61	–	–	1-PrOH	6.92	8.85	–	–
II		7.57	10.01	–	5.58		7.40	9.76		6.54
III		6.88	8.49	11.38	–		6.81	8.66	11.30	–
IV		7.42	9.35	11.53	–		7.11	9.53	11.56	–
V		5.61	8.25	11.24	3.73		5.50	8.30	11.19	3.68
I	90	7.19	8.76	–	–	2-PrOH	7.04	9.05	–	–
II		7.71	10.23	–	6.82		7.54	10.28		6.61
III		7.09	8.69	11.52	–		6.92	8.84	11.43	–
IV		7.61	9.59	11.60	–		7.20	10.13	11.65	–
V		5.79	8.42	11.34	3.81		5.73	8.46	11.28	3.81

Table 3 Continued

Schiff base	Et/%	pK_1	pK_2	pK_3	pK*	Solvent 70%	pK_1	pK_2	pK_3	pK*
I*	0	5.01	6.89	–	–	Acetone	7.73	9.41	–	–
II*		5.60	7.30	–	4.52		8.02	10.53		7.07
III*		4.81	7.61	9.17	–		7.43	9.08	11.60	–
IV*		5.47	7.32	10.28	–		7.92	10.40	11.54	–
V*		4.01	6.20	9.09	4.94		6.39	8.81	11.45	4.63
I*	100	7.46	9.01	–	–	DMSO	8.21	9.68	–	
II*		8.00	10.57	–	7.11		8.63	10.95		7.95
III*		7.39	8.98	11.78	–		7.83	9.54	11.74	–
IV*		7.89	9.87	11.81	–		8.51	10.65	11.86	–
V*		6.01	8.74	11.65	4.09		6.76	9.38	11.57	5.13

pK_1=pK_{OH} for OH at position 7, pK_2=pK_{OH} for OH at position 5, pK_3=pK_{OH} phenolic and pK*=pK_{COOH} (II) and pK_{SO_3H} (V). These are the mean pK_a values of the values obtained by interpolation for half $\bar{n}_A$ values and log term methods

*Values obtained from linear regression equation

$$pH = pK_a - \log[\text{salt}]/[\text{acid}] \tag{9}$$

The distribution fractions of the salt species:

$$\alpha_{\text{salt}} = [\text{salt}]/([\text{salt}] + 1) \tag{10}$$

and the distribution fractions of the acid species:

$$\alpha_{\text{acid}} = 1 - \alpha_{\text{salt}} \tag{11}$$

From the above relations, we can calculate the degree of distribution (α) of the unionized species α_{acid} and the ionized species α_{salt} for any polyprotic ligand, taking each ionization step as a separate step.

The calculated degrees of distribution for the Schiff bases under investigation (at 0.10 M NaCl, 25°C and 70% v/v EtOH–H_2O medium) demonstrate that H_2A and HA^- are the most predominant species for Schiff base I at pH 5.5 and 7.2, respectively. A^{2-} is the most predominant species at pH>9.8. For Schiff bases II, III and IV, H_3A is the most predominant species up to pH 5, while H_2A^- is the most predominant species at pH 6.8, 7.5 and 8, respectively. HA^{2-} is the most predominant species at pH 8.5, 9.2 and 10.3 for Schiff bases II, III and IV, respectively, while A^{3-} is the most predominant species at pH >10.9. For Schiff base V, H_4A, H_3A^-, H_2A^{2-} and HA^{3-} are the most predominant species at pH 2.2, 4.55, 6.8 and 9.6, respectively, while at pH >12.2, A^{4-} is the most predominant species. The points of intercept at which the degree of distribution of species H_4A is equal to that of H_3A^-, the degree of distribution of species H_3A^- is equal to that of H_2A^{2-}, the degree of distribution of species H_2A^{2-} is equal to that of HA^{3-}, and the degree of distribution of species HA^{3-} is equal to that of A^{4-} represent pK_1, pK_2, pK_3 and pK_4, respectively.

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