

Acid Dissociation Constants of Some Schiff Bases

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The acidity constants of eleven schiff bases have been evaluated potentiometrically in ethanol-water media of different compositions. The trend in the pK values of various schiff bases has been explained in terms of the nature of the substituent and the polarity of the medium.

Schiff bases have recently received much attention because of their use as models for biological systems. It was, therefore, of interest to determine the dissociation constants of some schiff bases of general structures (I and II) in water-ethanol media of different compositions potentiometrically.

The ligands were synthesized¹, by the condensation of the aldehyde (salicylaldehyde or naphthaldehyde) with the amine (diethylenetriamine, phenylhydrazine, monoethanolamine, *o*-aminopyridine, salicylhydrazide, *o*-aminophenol, *o*-phenylenediamine, ethylenediamine, propylenediamine, benzoylhydrazide and anthranilic acid).

Carbonate-free sodium hydroxide solution was prepared from AR grade NaOH and standadized against potassium hydrogen phthalate.

The electrometric titrations were carried out at 25°C using a precision laboratory pH-meter filled with calomel-glass electrode assembly. The instrument was calibrated as previously reported². Carbonate dioxide-free nitrogen gas was bubbled through the solution during the titration, to ensure stirring and a neutral atmosphere. The solution was magnetically stirred to improve the mixing of the solution.

Standard state hydrogen-ion activity was obtained after applying Van Uitert³ pH correction factor to the pH meter readings. All acidity and other equilibrium constants were calculated as concentration functions⁴⁻⁶. The pK_a values of schiff bases (I-11) in water-ethanol media of different compositions were obtained using Irving and Rossoti technique⁷. The formation curve was constructed by plotting the \bar{n}_A values (the number of protons attached to the ligand) against pH of the solution corresponding to each

addition of alkali. This method has been used fairly successfully in other systems in our laboratory (azo⁸⁻¹², nitroso¹³ and ethanolamines¹⁴).

The titration of compound (5) revealed that three protons are liberated and the stepwise equilibrium constants are given by the relations (1-3)

$$K_1 = [H^+][H_2A^-]/[H_3A] \quad \dots (1)$$

$$K_2 = [H^+][HA^{2-}]/[H_2A^-] \quad \dots (2)$$

$$K_3 = [H^+][A^{3-}]/[HA^{2-}] \quad \dots (3)$$

where $[H_3A]$, $[H_2A^-]$, $[HA^{2-}]$ and $[A^{3-}]$ represent concentrations of the undissociated ligand and the mono-, di- and tri-anions, respectively. The first and the second constants overlap but the third is well separated from the others. Values of K_1 and K_2 can be obtained from expression (4)

$$\frac{\bar{n}[H^+]}{(\bar{n}-1)} = K_1 K_2 \frac{(2-\bar{n}) - K_1}{[H^+](\bar{n}-1)} \quad \dots (4)$$

where \bar{n} is the average number of protons removed per molecule of the ligand. The value of \bar{n} was determined from a knowledge of the stoichiometry of the solutions, and $[H^+]$ was calculated from the experimentally corrected pH values using the relation:

$$[H^+] = \text{antilog}[-pH - \log \gamma_{H^+}]$$

where γ_{H^+} was assumed to be equal to $\gamma_{\pm}(\text{HCl})$ at the relevant ionic strength. The plot of the left hand side of Eq. (4) versus $2-\bar{n}/[H^+](\bar{n}-1)$ should be linear with a slope of $K_1 K_2$ and an intercept of K_1 , from which K_1 and K_2 can be calculated. The third constant, K_3 , was calculated from the relation (5),

$$pK_3 = \frac{(pH + \log \gamma_{H^+}) - \log([Na^+] - 2C - [OH^-])}{(3C - [Na^+] + [OH^-])} \quad \dots (5)$$

The $[OH^-]$ was found from the relation (6)

$$[OH^-] = \text{antilog}(pH - pK_w - \log \gamma_{\pm}) \quad \dots (6)$$

In Eq. (6) pK_w is the negative logarithm of the ionic product of water. The results of computations are collected in Table I.

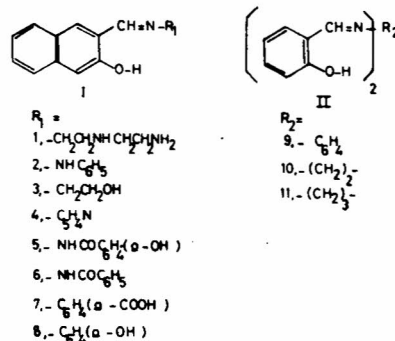


Table 1— pK_a Values for Some Schiff Bases at $25 \pm 0.1^\circ\text{C}$ in Water-Ethanol Media of Varying Compositions

Compd	% EtOH					
	50	60	70	80	90	100
1	9.90	10.00	10.22	10.33	10.43	10.61
2	—	11.22	11.66	11.53	11.17	10.76
3	10.11	10.20	10.33	10.45	10.80	10.96
4	8.85	9.53	9.83	9.95	10.00	—
5	8.83	9.11	9.32	9.54	9.84	9.86
	11.09	11.21	11.33	11.50	11.78	11.66
	11.96	12.12	12.25	12.38	12.50	12.67
6	10.30	10.39	10.50	10.75	10.81	—
	11.88	12.12	12.25	12.36	12.49	—
7	8.10	8.39	8.45	8.78	9.02	—
	8.60	9.40	9.50	9.80	9.55	—
8	8.55	8.90	9.22	9.50	9.80	—
	8.80	9.25	9.45	9.64	9.65	—
9	—	9.80	10.10	10.40	10.60	10.87
	—	10.68	10.20	10.98	10.03	11.07
10	—	10.47	10.84	11.00	11.37	11.46
	—	10.50	11.70	11.90	12.00	12.14
11	—	10.43	10.64	10.98	11.10	11.16
	—	10.85	11.50	11.66	11.95	12.05

All the compounds, except that derived from phenylhydrazine, gave the same trend in pK values, i.e. an increase in pK_a with increase in concentration of ethanol in the reaction medium. It has been reported that the dissociation of the carboxy group in glycine increases linearly with increase in concentration of the cosolvent while the dissociation of the substituted ammonium-hydrogen is non-linear and in most cases passes through a maximum (minimum pK_a) at some solvent composition¹⁵. The variation of pK_1 of glycine with solvent composition, as with carboxylic acids in general, can be explained by an electrostatic model based on the Born equation¹⁶. The cationic acids of ethylenediamine failed to follow this model, where both the solvent and the dielectric effects seemed to control this behaviour. The former is assumed to be greater in acids involving $=\text{NH}^+$ dissociation¹⁷. The non-electrostatic contribution to the change in pK_a has been regarded as representing the sum of medium effects for individual ions¹⁸. All the presently studied ligands possess azomethine linkage that is highly polarized. In general, there are few accurate measurements available on the basicity of imines, but they seem to be weaker bases than the corresponding amines. The lower pK_a values of the imines could be ascribed to two opposing effects: the change from sp^3 to sp^2 hybridization for the nitrogen atom, and the inability of the unshared pair of electrons on the nitrogen atom to overlap with the aromatic π -electrons. All the compounds gave a characteristic pK_a for the phenolic $-\text{OH}$ (~ 10). The probability of protonation of these compounds under the present

Table 2— W Values for Some Schiff Bases in Presence of Ethanol (obtained from $X-Y$ plot)

Compd	J	W	Compd	J	W
1	1	0.28	7	1	0.90, 1.20*
				2	0.64, 0.99*
2	1	1.14	8	1	0.95, 0.72*
	2	1.30		2	1.00, 0.33*
3	1	0.20	9	1	1.10
4	1	1.70		2	0.70
	2	1.30	10	1	1.10
5	1	0.63	11	1	1.20
	2	0.50		2	0.70
6	1	—			
	2	—			

The observed data are obtained from pK_1 values; those marked with (*) are obtained using the pK_2 values.

experimental conditions is of minor importance. The change of pK_a value of the weaker base, phenylhydrazine, in its schiff base is due to delocalization of the nitrogen lone pair electrons extending into the phenyl ring. Again the structural chemistry of the diethylenetriamine moiety of the schiff base compound plays a major part in controlling its behaviour, because of the electrostatic repulsion between the terminal protonated nitrogen atoms²⁰, leading to the probably to the existence of a zwitterion structure which is responsible for such data (Table 1). In our laboratory, extensive work has been done on the ethanolamine compounds^{14, 21-26}. The behaviour of such systems was explained on the basis of the presence of the hydrogen bond due to the relative polarizabilities of the proton donating group and the proton accepting group. This brought about a change in the oxygen lone pair dipole thereby leading to charge fluctuation in the more mobile N lone pair orbital¹⁹. The pK_a of the schiff base compound (3) could be ascribed to the phenolic $-\text{OH}$ rather than to the alcoholic $-\text{OH}$. On the other hand, the relatively lower pK_a value of *o*-aminopyridine based schiff base compound parallels the high basic property of the *o*-aminopyridine moiety (Table 1). The data for the hydrazide compounds are interesting. The pK_a values of some hydrazides depict that they are much weaker bases because of the conjugative electron withdrawing group attached to the hydrazino system¹⁹. The semicarbazones are weaker bases than semicarbazide itself because of the change in hybridization of the nitrogen atom. The sp^3 nitrogen atom of the hydrazones interacts substantially with the groups attached to the carbon atom¹⁹. Three pK_a values have

been evaluated for the compound (5), while compound (6) gives two pK_a values. The lower pK_a values for 6 in comparison to those for 5 could be due to the existence of an intramolecular hydrogen bond between $-C=O$ and $-OH$ groups. On the other hand, the third pK value for 5 points to the existence of keto-enol equilibria in such compounds. The second pK for 6 could also arise because of keto-enol equilibrium. Compound (7) gives two pK_a values: the lower one is due to the ionization of the carboxy group while the higher one is due to the ionization of the hydroxy group. The closeness of the two pK values of 8 permits us to apply Eq. (4). Following our argument on compounds of type (II), one can correlate the obtained pK data with the geometry and the chain length of the prepared compounds. In all the compounds derived from ethylenediamine, propylenediamine and *o*-phenylenediamine two pK values are obtained. In general as the chain length of the amine increases, the pK values decrease. The lowest pK values are obtained in the case of compounds derived from *o*-phenylenediamine. This is probably due to the presence of substituted phenyl groups (Table 1).

To explain the effect of varying alcohol content of the reaction medium on the dissociation constants in a more quantitative manner, the following could be assumed: if the J -factor represents a solvent number characteristic of the tested chemical reaction or part of it could be attributed to the transfer of the co-solvent, the following equation (Eq. 7) can be applied¹⁴:

$$J \log[S] + \log K_1 = \frac{-\Delta G}{2.3 RT} - W \left(\frac{[H_2O]_s}{[S]} + J \log[H_2O] \right) \quad \dots (7)$$

In Eq. (7) J and W are unknown parameters; $[S]$ is the concentration of the solvent used. The other terms have their usual meaning. To simplify, the left hand side Eq. (7) (designated as X) is plotted against $[H_2O]_s/[S]$ (designated as Y). A linear plot should be obtained, the slope of which should give the value of W (W represents the number of water molecules taking part in the reaction) (Table 2). Different trials were done with different J -values (Table 2). It is observed

that when the value of J approaches that of W , solvation plays only a minor role. Very small pK values have been obtained for 1, 3 and 6 where aquation is very low. The solvation is apparent in systems where the J -value is assumed to be 2. Under the latter conditions, the W -values are less than those of J , due to solvation (Table 2).

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