

THERMODYNAMICS OF 1,10-PHENANTHROLIUM ION IN ETHANOL-WATER

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ABSTRACT

Dissociation constants of the 1,10-phenanthrolium ion in different aqueous ethanolic solutions have been determined spectrophotometrically and pH-metrically. Some aspects of the role of the solvent have been discussed.

INTRODUCTION

The ligand 1,10-phenanthroline is widely known for its analytical applications. A large number of workers have determined the dissociation constant of the ligand and its complexes in aqueous solutions¹. The thermodynamics of 1,10-phenanthroline and its iron(II) complex have been determined by the present authors². However, little attempt has been made to determine the dissociation constants of the 1,10-phenanthrolium ion in solvents other than water. Such studies would be useful in elucidating the role of solvents on the dissociation constants of the 'isoelectric' reactions of the type $AH^+ \rightleftharpoons A + H^+$ which is known to be little affected by the change in dielectric constants³.

In order to explore the role of the solvents and to have some idea regarding the solute-solvent interactions, we determined the dissociation constants of the 1,10-phenanthrolium ion in different aqueous ethanolic solutions spectrophotometrically and pH-metrically. We also present the thermodynamics of the ligand in aqueous ethanolic solutions based on the enthalpy data determined calorimetrically in this laboratory⁴.

EXPERIMENTAL

Absolute ethanol was treated with an excess of calcium oxide, kept overnight and distilled. The middle fraction was collected for use. The traces of water content, if any, in the organic solvent were neglected.

Perchloric acid, caustic soda, acetic acid used were of reagent grade. The stock solution of the ligand was prepared by dissolving the weighed amount of 1,10-phenanthroline hydrate (E. Merck) in the desired solvent. The solutions were prepared using double-distilled water from an all-glass apparatus.

The weight-percentages of the organic solvent in mixed solvents were determined by mixing the calculated amounts of the two solvents by volume. The reliability of this method of preparing a solvent mixture of given composition was checked by determining its density and comparing it with the reported density values⁵.

For the dissociation constants of the ligand in different percentages of the mixed solvents, sodium acetate and acetic acid buffers as well as perchloric acid solutions were used.

Since the actual activity coefficients are difficult to determine particularly in mixed solvents, the measurements were taken in solutions of very low ionic strength (10^{-3} – 10^{-4} M) so that the dissociation constant values may be taken as thermodynamic values.

The ligand is known to absorb strongly in the UV region. The position of the absorption maxima of the ligand changes with the pH of the solutions. The absorption maxima of the ionic and molecular forms were found to be 272 and 264 nm, respectively. The absorption maxima do not change even in 90% v/v alcohol.

For the determinations of pK values of the ligand in different mixed solvents, the optical density readings of the ligand in excess acid and in excess alkali and at intermediate pHs were taken at 255 and 260 nm, as at these wave lengths the difference in optical densities of the two species is maximum. All care was taken to improve the accuracy in measurement, although the authors are aware that the

TABLE I

DISSOCIATION CONSTANTS OF 1,10-PHENANTHROLINE IN AQUEOUS-ETHANOL SOLUTIONS

Temp. = 25°C.

<i>Wt. % of organic solvent</i>	<i>D</i>	<i>I/D × 10²</i>	<i>Mole fraction of the organic solvent</i>	<i>pK (from spectrophotometry)</i>	<i>pK (from pH-metry)</i>
0	78.56	1.27	—	5.05	—
8.0	74.04	1.35	0.033	4.90 (±0.03)	4.82 (±0.03)
16.4	70.59	1.42	0.071	4.75 (±0.03)	4.70 (±0.04)
25.3	65.52	1.53	0.117	4.50 (±0.04)	4.41 (±0.04)
34.4	58.51	1.71	0.170	4.34 (±0.05)	4.27 (±0.05)
44.0	52.73	1.90	0.235	4.05 (±0.05)	4.03 (±0.05)
54.1	46.87	2.14	0.315	3.82 (±0.06)	3.89 (±0.06)
64.7	40.95	2.45	0.418	3.68 (±0.06)	3.77 (±0.06)
76.0	34.35	2.92	0.554	3.62 (±0.08)	3.70 (±0.08)
87.6	29.31	3.41	0.734	3.70	—

accuracy of the pK values determined ultimately depends on the accuracy of the determination of H^+ ion concentrations in mixed solvents.

To assess the accuracy of the pK values of the ligand obtained by the spectrophotometric method, the pK values of the ligand were determined by pH titration also. For the determination a definite amount of the ligand in different volumetric flasks was neutralised to different extents (30 to 70% neutralised) with known quantities of perchloric acid and the meter readings were taken. The experiment was repeated with different concentrations of the ligand. The average pK values are given in Table 1.

Spectrophotometric readings were taken with a Beckman DU spectrophotometer. The pH meter readings were taken with a Cambridge bench type battery operated pH meter. All the readings were taken at 25°C.

RESULTS

The thermodynamic dissociation constant K_T for the equilibrium $AH^+ \rightleftharpoons A + H^+$ ($A = 1,10$ -phenanthroline) is

$$K_T = \frac{a_A \times a_{H^+}}{a_{AH^+}} = \frac{C_A \cdot C_{H^+}}{C_{AH^+}} \times \frac{f_A \cdot f_{H^+}}{f_{AH^+}}$$

In our measurements, the hydrogen ion concentrations are of the order 10^{-3} – 10^{-4} M and the ionic strengths of the solutions were of the order 10^{-3} M (even if acetate buffers were used); therefore $f_A \times f_{H^+}/f_{AH^+}$ can be taken to be unity.

$$\text{Thus, } pK_T = pH^* + \log \frac{C_{AH^+}}{C_A}$$

$$= [B] + \log U_H + \log \frac{C_{AH^+}}{C_A}$$

$$= [B] + \log U_H + \log \frac{d_M - d}{d - d_1}$$

where $[B]$ = meter reading in mixed solvents; $\log U_H$ = correction factor in mixed solvents; d_M , d_1 and d are optical densities of the ligand in the molecular form, ionic form and at intermediate pHs.

Knowing $[B]$, $\log U_H$, d_M , d_1 and D values at different percentages of the mixed solvents, pK_T values were determined.

For the determination of pK by pH-metry, $\log C_{AH^+}/C_A$ was determined from the fraction of neutralisation. The dielectric constant values of different ethanol-water mixtures were calculated from the data of Akerlof and Short⁶. The glass electrodes in different mixed solvents were calibrated in the same way as described earlier⁷⁻⁹ and $\log U_H$ (correction factor) values were determined before each set of measurement.

DISCUSSION

The pK values of the 1,10-phenanthrolium ion in different ethanol-water mixtures are given in Table I.

(a) The pK values of the ligand are found to be a linear function of ethanol (up to 60% by weight) (Fig. 1).

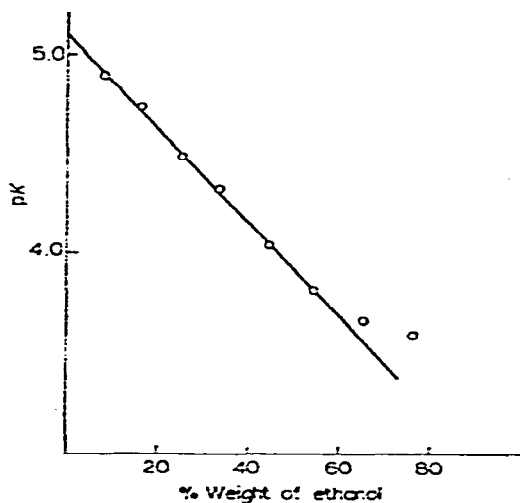


Fig. 1. pK against wt.% of ethanol.

(b) We plotted pK against mole fractions of organic solvents and obtained a linear curve (up to 60% by weight) similar to the observations of Van Uitert and Haas⁷ (Fig. 2).

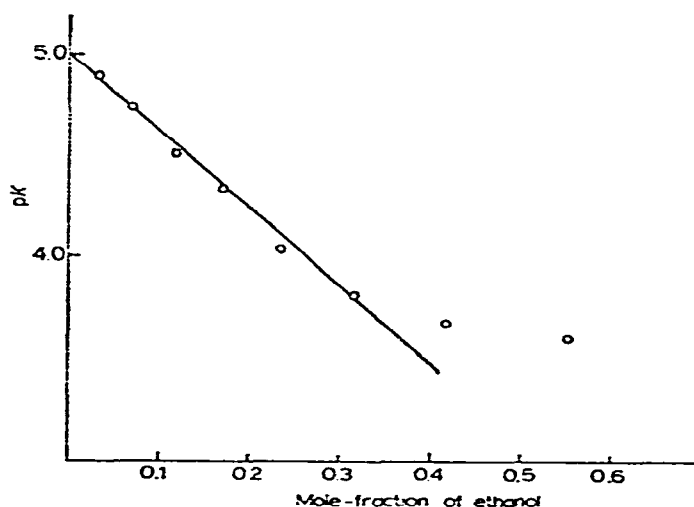


Fig. 2. pK against mole-fraction of ethanol.

(c) As observed by Wynne-Jones¹⁰, it has also been found in the present work that the dielectric constant in the region of 30 to 80 is a better correlating factor.

The plot of pK vs. $1/D$ gives a straight line up to 60 wt.% of ethanol, beyond which there is a deviation (Fig. 3). Deviation at a higher percentage of organic solvents may be due to the fact that at these high percentages of organic solvents, the H^+ ion values from pH meter reading may be inaccurate due to: (i) high liquid junction potential and (ii) low sensitivity of the glass electrode.

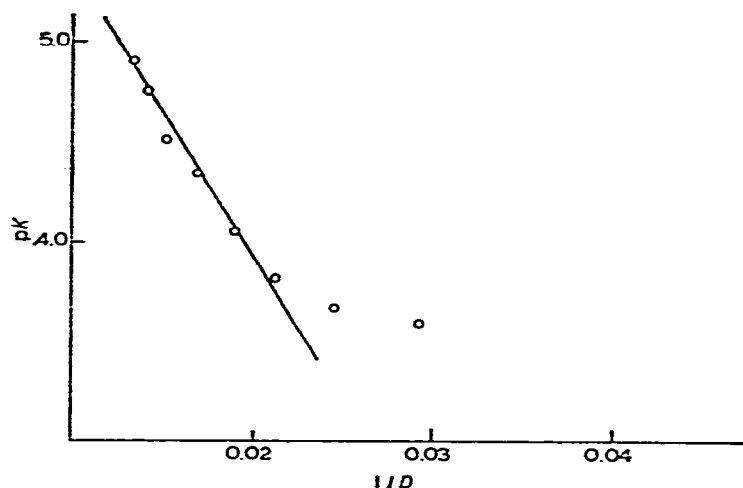


Fig. 3. pK against $1/D$.

The values at zero percent of organic solvent from these different type of extrapolations come out to be (a) 5.08, (b) 4.98 and (c) 5.00 in close agreement with our value of 5.05 in water².

It is interesting to note the change in the dissociation constants of the ligands due to the addition of organic solvents which decrease the dielectric constants. For the isoelectric reactions of the type $PhH^+ \rightleftharpoons Ph + H^+$ the dissociation constant of the reaction should be practically insensitive to the change of dielectric constant of the medium. The observed values of $p_s(K) - p_w(K)$ are large which indicate that solute-solvent interactions are much more pronounced than electrostatic effects³.

The results show that the pK value decreases slowly with increasing organic solvents, reaches minimum near about 65–75 wt.% of organic solvents and then increases again similar to the observations by Paabo et al.¹¹ and Ohtaki¹².

pK values give a measure of the change in free energies ($\Delta G_t = 2.303 RT \Delta pK$) on transferring the ligand from water to the mixed solvent medium. We have shown earlier¹³ that the determination of solvent basicity from the free energy of transfer is difficult. This involves a number of complicated terms as follows :

$$\begin{aligned} \Delta G_t^\circ &= \Delta G_s^\circ - \Delta G_w^\circ \\ &= \Delta G_{el(H^+)}^\circ + \Delta G_{el(PhH^+)}^\circ + \Delta G_{neut}^\circ + \Delta G_{ion-solv.}^\circ + \Delta G_{solv-solv.}^\circ + \Delta G_{basicity}^\circ \end{aligned}$$

It is possible to calculate $\Delta G_{ei(H^+)}^\circ$ and $\Delta G_{ei(PhH^+)}^\circ$ with the help of the well-known Born equation¹⁴ or improved equations due to Hepler¹⁵ and Stokes¹⁶, provided accurate values of the radii of the ions are known. However, in view of the non-availability of accurate values of the ions and other data (e.g. ΔG_{neut}°), we did not attempt to separate the free energy change into electrostatic and non-electrostatic parts. For a clear understanding of the role of the solvents on the dissociation constants of electrolytes, proper emphasis should be given to the theoretical and experimental determination of ion-solvent interactions in different mixed solvents. For this it is necessary to have more data on the dissociation constants of electrolytes and also on the radii of the respective ions in different mixed solvents.

Recently, enthalpy data for the reaction, $PhH^+ \rightleftharpoons Ph + H^+$, in different EtOH-H₂O solvents have been determined in this laboratory calorimetrically⁴. These values of ΔH and those of ΔG reported in the present work give the values of ΔS . All these thermodynamic quantities for the reaction, $PhH^+ \rightleftharpoons Ph + H^+$, in different aqueous-ethanolic solutions are presented in Table 2.

TABLE 2

THERMODYNAMICS FOR THE REACTION $PhH^+ \rightleftharpoons Ph + H^+$

<i>Wt. % of organic solvent</i>	$\Delta G^\circ (\pm 0.05)$ <i>(interpolated value)</i> <i>in kcal</i>	$\Delta H^\circ (\pm 0.1)$ <i>in kcal</i>	$\Delta S^\circ (\pm 0.5)$ <i>in e.u.</i>
0	6.89	4.07	-9.5
10	6.62	4.30	-7.8
20	6.31	4.57	-5.9
30	5.98	4.32	-5.6
45	5.51	3.75	-5.9
60	5.04	3.45	-5.4

The results in Table 2 show that although ΔG° decreases continuously, ΔH° values increase on addition of ethanol reaching a maximum at about 20 wt.% of ethanol and then decrease again. The ΔS° values do not show any such trend. On addition of alcohol to water up to 20% a decrease is observed after which ΔH° remains practically constant.

The interpretation of thermodynamic data is extremely complex in view of our lack of knowledge of the structure of liquid mixtures and the extent of ion-solvent interactions. For the mixture of alcohol and water the excess free energy of mixing which is positive and nearly symmetrical at about $x_2 = 0.5$ ($x_2 =$ mole fraction of ethanol), is comprised of a negative and unsymmetrical enthalpy (minimum at $x_2 = 0.2$) and a positive entropy of mixing (maximum at $x_2 = 0.35$)¹⁷. PhH^+ ion, because of its size, has little chance of solvation while the H^+ ion will be solvated to a large extent. As such the solvation of the proton in the different mixed solvent media

may play a major role leading to the changes in the values of the thermodynamic quantities. For any definitive explanation extensive data in mixed solvent would be needed.

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