

free metal ion, ligands and binary complex. The higher activity shown by mixed ligand complexes may probably be attributed either to the combined bio-active effects of both the ligands present in the chelate or due to their increased liposoluble nature as a result of coordination to the metal ion. Besides these factors the rapid diffusion of the metal complex through the cell-membrane of fungi and bacteria may be one of the important factors.

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Potentiometric Determination of Ionization Constants of 3-Phenyl-1-(2'-hydroxyphenyl)-2-propen-1 ones

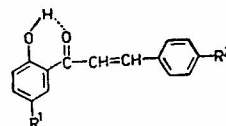
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The ionization constants of 3-phenyl-1-(2'-hydroxyphenyl)-(PHPO)-, 3-phenyl-1-(2'-hydroxy-5'-methylphenyl)-(PHMPO)-, 3-phenyl-1-(2'-hydroxy-5'-chlorophenyl)-(PHCPO)-, 3-phenyl-1-(2'-hydroxy-5'-bromophenyl)-(PHBPO)-, 3-phenyl-1-(2'-hydroxy-5'-nitrophenyl)-(PHNPO)- and 3-(4''-methoxyphenyl)-1-(2'-hydroxyphenyl)-(MPHPO)-2-propen-1-ones have been evaluated potentiometrically at different temperatures, ionic strengths and in solutions of varying dielectric constants. The order of ionization constants is : PHMPO > MPHPO > PHPO > PHBPO > PHCPO > PHNPO. The Hammett's and Born's equations are found to be applicable. The isokinetic temperatures in the range 320-325 K (experimental temperature = 308° K) in all the cases indicate that the process of ionization is enthalpy-controlled.

IN continuation of our earlier work¹⁻³, we report in this note the ionization constants of 3-phenyl-1-(2'-hydroxyphenyl)-(PHPO)-, 3-phenyl-1-(2'-hydroxy-5'-methylphenyl)-(PHMPO)-, 3-phenyl-1-(2'-hydroxy-5'-chlorophenyl)-(PHCPO)-, 3-phenyl-1-(2'-hydroxy-5'-bromophenyl)-(PHBPO)-, 3-phenyl-1-(2'-hydroxy-5'-nitrophenyl)-(PHNPO)- and 3-(4''-methoxyphenyl)-

1-(2'-hydroxyphenyl)-(MPHPO)- 2-propen-1-ones, determined potentiometrically at different temperatures and in media of varying dielectric constants and ionic strengths.



	R ¹	R ²
PHPO	-H	-H
PHMPO	-CH ₃	-H
PHCPO	-Cl	-H
PHBPO	-Br	-H
PHNPO	-NO ₂	-H
MPHPO	-H	-OCH ₃

The compounds PHPO, PHMPO, PHCPO, PHBPO, PHNPO and MPHPO were prepared by the literature method⁴⁻⁸, recrystallized from ethanol and their purity checked by TLC and melting point determinations. The solutions of these compounds were prepared in required amounts of absolute ethanol. All other chemicals used were of AR grade. The solutions of nitric acid and KNO₃ were prepared in CO₂-free doubly distilled water.

An ELICO digital pH-meter model LI-120 with glass and calomel electrodes (accuracy ± 0.01 unit) was used for pH measurements and standardized with buffers of pH 4.00 and 9.20. The pH values in all aquo-organic mixtures were corrected using the method of Van Uitert and Haas⁹. Volume correction was applied by the method suggested by Rao and Mathur¹⁰.

The following solutions were titrated against carbonate-free NaOH solution at three different temperatures :

- (a) 10 ml of 1M KNO₃ + 70ml EtOH + 10 ml of 0.1M HNO₃ + 10 ml H₂O and (b) 10 ml of 1M KNO₃ + 60 ml EtOH + 10 ml of 0.1M HNO₃ + 10 ml of 0.01 M compound in 100% EtOH + 10 ml H₂O against 0.5 M NaOH and
- (ii) 10 ml of 1M KNO₃ + 60 ml EtOH + 10 ml of 0.01M compound in 100% EtOH + 20 ml H₂O against 0.1M NaOH. The effects of dielectric constant and ionic strength were studied by determining the pK_a values in solutions of varying concentrations of ethanol and KNO₃ respectively.

The ionization constants were calculated using Bjerrum-Calvin pH titration technique as adopted by Irving and Rossotti¹¹. The ionization constants obtained by solving formation function were found to be in good agreement with the values calculated from the Henderson's equation (Table 1). The uncertainty in the pK_a values is of the order of ±0.02. The pK_a values of the phenols follow the decreasing order : PHMPO > MPHPO > PHPO > PHBPO > PHCPO > PHNPO.

The order of the ionization constants of the acids can be explained based on the strength of the hydrogen

NOTES

TABLE 1 — IONIZATION CONSTANTS OF SUBSTITUTED PHPOs AT DIFFERENT TEMPERATURES

[Solvent : Aq. EtOH (70% v/v); $\mu = 0.1M$ (KNO₃)]

Compound	pK_a at		
	35°	45°	55°
PHPO	(10.63) 10.65	10.55	10.46
PHMPO	(11.10) 11.10	10.80	10.48
PHCPO	(10.20) 10.10	9.83	9.68
PHBPO	(10.55) 10.50	10.27	10.08
PHNPO	(9.32) 9.25	9.03	8.84
MPHPO	(10.88) 10.80	10.72	10.65

Values in parenthesis obtained from Henderson's equation.

TABLE 2 — VALUES OF THE CONSTANTS A, B AND C AND THE THERMODYNAMIC PARAMETERS

Compound	A	B	C	+ΔG kcal/ mol	+ΔH kcal/ mol	-ΔS e.u. at 35°
PHPO	1636.7	3.20	0.007	15.01	4.58	33.85
PHMPO	-3273.3	41.25	-0.006	15.64	12.54	10.08
PHCPO	3273.3	-4.04	0.012	14.23	10.03	13.64
PHBPO	6546.6	-24.24	0.044	14.80	10.95	12.49
PHNPO	4909.9	-15.34	0.028	13.04	10.27	8.97
MPHPO	1636.7	2.81	0.009	15.22	3.71	37.36

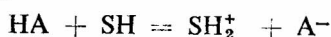
bond formed between the phenolic hydrogen and the carbonyl oxygen. The electron withdrawing group in the para-position as in the case PHNPO, PHCPO, and PHBPO weaken the hydrogen bond, thereby facilitating the easy liberation of phenolic proton in solution, as a result the pK_a is less than that of PHPO (unsubstituted).

The electron releasing group in para- position (as in PHMPO) strengthen the hydrogen bond thereby rendering the ionization less facile and consequently its pK_a is greater than PHPO. The substitution of the methoxy group (e. g. in MPHPO) in the second ring has very little effect on the ionization, hence the change in pK_a is less.

The linear relation between pK_a and σ (σ being taken from literature¹²) indicates that ionization proceeds by a similar mechanism in all the acids. The pK_a values decrease with increase in temperature indicating that the process of ionization is endothermic. pK_a value is related to the absolute tem-

perature by the relations : $pK_a = A/T + B + CT$, where, A, B and C are constants. The values of A, B and C have been evaluated for different ligands (Table 2). The thermodynamic parameters ΔG , ΔH and ΔS were evaluated from the above constants using the following relationships- $\Delta H = 2.303R(A - CT^2)$ $\Delta G = 2.303R(A + BT + CT^2)$; and $\Delta S = 2.303R(-B - 2CT)$ and the values so evaluated are given in Table 2. The uncertainty in the values of ΔH and ΔG is found to be of the order of ± 0.5 kcal/mol, and in ΔS it is ± 2 e.u.

The negative entropy values of the ionization of phenolic OH can be explained by considering the equilibrium



The change in entropy is given by Eq. (1).

$$\begin{aligned} \Delta S &= (S_{SH_2^+} + S_{A^-}) - (S_{HA} + S_{SH}) + \Delta S_{\text{soliv.} \rightarrow \text{soliv. Inter.}} \\ &= (S_{SH_2^+} - S_{SH}) + (S_{A^-} - S_{HA}) + \Delta S_{\text{soliv.} \rightarrow \text{soliv. Inter.}} \\ &= X + Y + \Delta S_{\text{soliv.} \rightarrow \text{soliv. Inter.}} \dots(1) \end{aligned}$$

In Eq. (1) the first two terms should be negative, since ions carrying a charge must be highly solvated resulting in the decrease of entropy with respect to neutral molecules. $\Delta S_{\text{soliv.} \rightarrow \text{soliv. Inter.}}$ depends on the fraction of the organic component and its ability to stabilize or destabilize the water structure^{13,14}.

The isokinetic temperatures (β) of the ionization of phenols calculated by plotting ΔH against ΔS come out to be in the range of 320-325 K. These are above the experimental temperature of 308° K, indicating that the process of ionization is enthalpy-controlled.

The pK_a values of the compounds in solutions of varying dielectric constants are given in Table 3. The plots of pK_a vs n (the mole fraction of ethanol) for different ligands are linear with almost identical slopes (1.6 to 1.7) indicating that the ionization of all the compounds proceeds by the same mechanism. Born's equation is found to be applicable, as is evident from the linear plot of $-\log K_a$ versus $1/D$.

The ionization constants of all the compounds decrease with increase in ionic strength (Table 3). This may be explained as follows : The equilibrium constant (K_a) for the above ionization process can be written as —

$$K_a = \frac{[H^+][A^-]}{[HA]} \cdot \frac{f_{H^+} f_{A^-}}{f_{HA}}$$

TABLE 3 — IONIZATION CONSTANTS OF SUBSTITUTED PHPOs AT DIFFERENT IONIC STRENGTHS AND DIELECTRIC CONSTANTS AT 35°

Compound	pK_a at different								
	Ionic strengths					Dielectric constants			
	0.00	0.05	0.10	0.15	0.20	48.20	44.00	39.60	37.80
PHPO	10.82	10.72	10.65	10.52	10.42	10.40	10.65	10.78	10.90
PHMPO	11.32	11.21	11.10	10.96	10.82	11.00	11.10	11.46	11.60
PHCPO	10.42	10.27	10.10	9.95	9.82	9.80	10.10	10.35	10.48
PHBPO	10.88	10.66	10.50	10.36	10.19	10.26	10.50	10.72	10.85
PHNPO	9.58	9.42	9.25	9.10	8.92	9.06	9.25	9.44	9.57
MPHPO	11.10	10.95	10.80	10.65	10.51	10.62	10.80	11.03	11.20

In the secondary salt effect, the added salt not only influences the activity coefficients but also the concentrations of H^+ , A^- and HA . The activity coefficient of a neutral molecule (f_{HA}) is only slightly influenced by the ionic strength, but f_{H^+} and f_{A^-} are both decreased by increasing the ionic strength¹⁵. The net result is therefore, an increase in the degree of dissociation or decrease in pK_a .

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2-Thiopyrogallol—A New Sensitive & Selective Photometric Reagent for Determination of Tungsten

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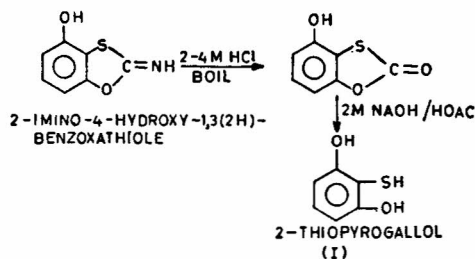
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2-Thiopyrogallol is reported as a new reagent for extractive photometric determination of trace amounts of tungsten. It is sensitive and selective photometric reagent and produces a violet complex with tungsten solution in the acidic pH range. The violet complex, extracted in the optimum pH range (0.8-2.0) using *iso*-amyl alcohol, absorbs at 500 nm. The system obeys Beer's law in the range 2-22 ppm with an optimum range 6-22 ppm metal. The molar absorptivity and Sandell's sensitivity values are 4.4×10^3 litre mol⁻¹ cm⁻¹ and 0.042 μ g cm⁻² W(VI) at 500 nm. 25-Fold excess of Fe(III) and Cr(III) and many other ions does not cause interference. The stepwise and overall stability constants of the 1:2 complex have been evaluated by photometric method.

TUNGSTEN is an important constituent in many of the geochemical materials¹, alloys²⁻⁴ and bio-materials. Toluene-3,4-dithiol⁶⁻¹⁰ has been used very often for analysis of such complex mixtures in chemical and geochemical prospecting. However, the previously reported method is not very satisfactory from the view points of suitable pH range, sensitivity, narrow optimum range of determination apart from the solubility and stability of reagent in aqueous solution. A new thiol reagent, 2-thiopyrogallol (I), has been developed as a photometric reagent for the determination of trace amounts of tungsten (VI). The reagent gives a violet coloured complex in the acidic medium.

A Hilger-Uvispek spectrophotometer with 1 cm glass cells was used. A systronics pH-meter (324, India) was used for all pH measurements. A known amount of sodium tungstate (E. Merck) was dissolved in doubly distilled water and the solution standardised by the oxine method¹¹. Solutions of diverse ions were prepared using AR grade salts and standardised by conventional methods.

Preparation of reagent solution—The reagent 2-thiopyrogallol was synthesised by the method of Pantlitschke and Benger¹². Resorcinol, copper sulphate and ammonium thiocyanate were mixed and the filtrate was neutralised with alkali; the precipitated benzoxathiole was hydrolysed with 4 M HCl to get 4-hydroxy-1, 3(2H)-benzoxathiole-2-one. It was dissolved in 0.1 M NaOH under N₂ at 60°C, warmed for 10 min and cooled, neutralised with acid. Thus, the aqueous solution of 2-thiopyrogallol was obtained *in situ* (Scheme 1). It was found to be stable for six hr. A 0.5% freshly prepared solution was always used for spectrophotometric investigations.



Scheme 1

Procedure—An appropriate amount of tungsten solution was taken in a 50 ml separatory funnel. A 0.5% aqueous solution of reagent (4 ml) was added followed by the addition of requisite amount of 1M hydrochloric acid to maintain pH at 1.5 of the 15 ml aqueous phase. The contents were mixed thoroughly. The red-violet tungsten complex was extracted for 5 min with one 10 ml and two 5 ml portions of *iso*-amyl alcohol. The combined extract was dried over anhydrous sodium sulphate and the solution transferred to a 25 ml volumetric flask. Volume was made up by adding pure *iso*-amyl alcohol. The absorbance of the violet complex was measured at 500 nm against solvent blank. A calibration curve was constructed for determining unknown metal strength.