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DETERMINATION OF IONIZATION CONSTANTS OF TRIS (TYDROXYMETHYLAMINOMETHANE) AT DIFFERENT TEMPERATURES AND IN MIXED SOLVENT SYSTEMS

Saeeduddin, A.W.K. Khanzada* and M.B. Rind**
Shah abdul Latif Government Degree College, Mirpurkhas, Sindh, Pakistan

Abstract

Ionization constants of tris is being studied at different temperatures from 20 to 50°C at 5°C interval and in 10,20,30 and 40 percent v/v dioxane water, methanol-water and ethanol-water solvent systems. Themodynamic parameters that are Gibb's free energy (Δ G), enthalpy (Δ H) and entropy (Δ S) at different temperatures also been studied. Results shows, pk_a values in mixed (organic-water) solvent system are higher than in aqueous media.

Introduction

We aimed to to study the effect of temperature and effect of organic-water solvent system on pk values of tris.

The ionization constants of weak acids and bases are widely used in pharmaceutical industries, spectroscopy, biological sciences, preparative chemistry and in structure elucidation of newly isolated species [1,2}.

There are different methods [3-7] which are being used for the determination of ionization constants of weak acids and bases. These methods have certain limitations, such as solubility, range of pk_a, time requirements etc. [5-8]. Although spectrophotometry is very accurate methal but it is time consuming.

The potentiometric titration has been improved by elimination of carbon dioxide by using dried and purified nitrogen values were obtained by analysing the experimental data with a computer program written in GW.BASIC to work on IBM; PC or compatible computers.

Experimental

* *National Centre of Excellence in Analytical Chemistry, University of Sindh, 78060, Sindh Pakistan.*

** *Institute of Chemistry, University of Sindh, Jamshoro, 78060, Sindh, Pakistan.*

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All chemicals were of anlytical grade and were used without further purification. Doubly degassed distilled water was used in preparation of all solutions. Fresh and distilled water was used in preparation of all solutions. Fresh and distilled dioxane, methanol and ethonal were used. Stock solution of 0.1M tris in water and 0.1M HCl containing 10, 20, 30 and 40% dioxane, methanol and ethanol were prepared. Stock solution of 0.01M tris in water was also prepared. The potentiometric titrations were performed in a thermostated double walled glass cell containing 50 ml of sample solution with HCl. The pH was determined with Philips PW 9420 digital pH meter which was coupled with Ingold combined glass and reference electrods dipped in sample solution whose temperature was controlled by circulating water through the jacket of measuring cell, JULABO HC thermostated bath accurate to ± 0.1 °C was used for controlling the temeprature. Prior to experiment the glass electrode was calibrated with 0.05M potassium hydrogen phthalate (pH at 25°C = 4.005) and 0.01M sodium tetraborate (pH at 25°C = 9.18) in respective organic water mixture. Sample solution was kept mixed by stirring with magnetic stirrer and inert by bubbling nitrogen gas which was dried and purified by passing through Fiser's solution [3]. For dispensing titrant. Mettler burette DV-10 acurate to 0.01 ml was used. The potentiometric measurements were performed on sample solution at different temeprature and in different solvents and solvent composition.

The potentiometric data was analysed by a computer program, written in GW-BASIC for calculation of ionization constants of nonacidic, bases (tris)

Results and Discussion

The ionization constant of tris were determined in aqueous media at 20, 25, 30, 35, 40, 45 and 50 °C and in 10,20,30, 40% organic water solvent mixture at 25°C. Experimental data obtained was treated with computer program in GW-BASIC for monoacidic bases.

The pk_a values obtained are presented in Table I with reported results. This table listed pk_a (concentration ionization constant pk_a. thermodynamic ionzation constant and thermodynamic constant ΔG, ΔH & ΔS).

Increase in temperature causes decrease in pk values but this decrease is not same. Closer inspection of fig. I further shows that the decrease is somewhat gradual except between 40 to 45°C. When temprature increase from 20 to 25°C then decrease in pk_a value is 0.123 unit while between 25 to 30°C, is 0,142 unit, between 20 to 35°C, it is 0.110, between 35 to 40°C it is 0.116 between 40 to 45°C it is 0.216 (quite higher), again between 45 to 50°C, it is 0.175 unit.

Fig.2 shows the effect of temperature on Gibb's free energy is observed when temperature increase from 20 to 50°C. Sharp decrease is seen when temperature increases from 40 to 50°C.

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In recent years many non-aqeous solvents have been increasingly used in analytical chemistry. They are generally organic solvents, and may be used as mixture, with each other or with water. For this reason it is interesting to compare their behaviour with that of water. One of the most important property of a solvent is its dielectric constant, which define, to a considerable degree of the solvating ability of the medium [11].

We choosed three solvents (dioxane, methanol and ethanol). Selection of these solvents, based on the fact that methanol and ethanol are the solvents having close dielectric constants values 32.6 and 24.3 respectively and also having ability to form hydrogen bonds while dioxane has dielectric constant value 2.21 but have no ability to form hydrogen bonds.

There is considerable difference in the solvating of the two groups. In order to measure the effect of the groups on pk_a values of tris we extended our investigation. The influence of the nature of the solvent and composition of the medium on ionization equlibria was studied.

Fig.3 shows the effect of mixed solvent mixtures (dioxane water, methanol water and ethanol water) on pk_a values of tris. Pk_a values generally increases as composition of organic solvent increases from 10 to 40 percent. This figure further shows that pk_b values of slowly increases in dioxane-water and EtOH-water as composition increases from 10 to 40% but in methanol-water sharp increase is marked when composition of organic solvent increases from 10 to 20%.

These figure clearly indicate that the pk_b values in dioxane water solvent mixutre are much higher thatn in methanol water and ethanol-water solvent mixtures. The reason is that the dielectric constant value of dioxane is 2.21 while for methanol and ethanol is 32.6 & 24.3. The marked diference between these values is responsible for difference between pk values.

Fig. 4 show the effect of organic water solvent mixture on Gibb's free energy (ΔG). As composition increase from 10 to 40, then G values also increases monotonically,

Above finding leads us to conclude that temeprature and solvent nature has significant effect on pk values.

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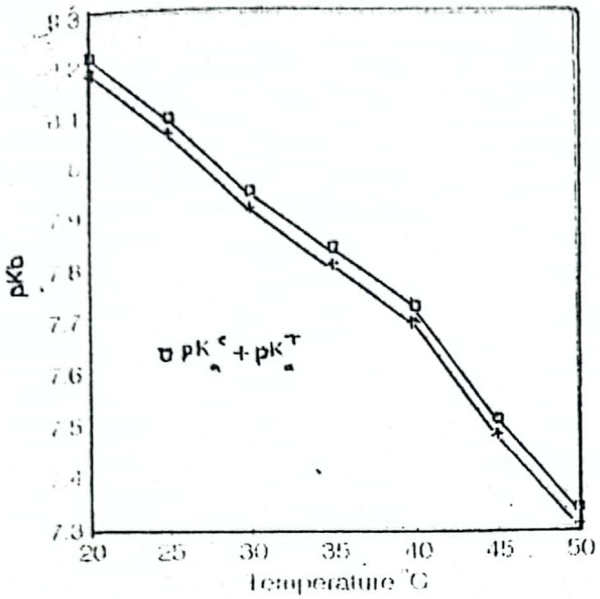


Fig.1 Effect of temperature on pKb values of tris.

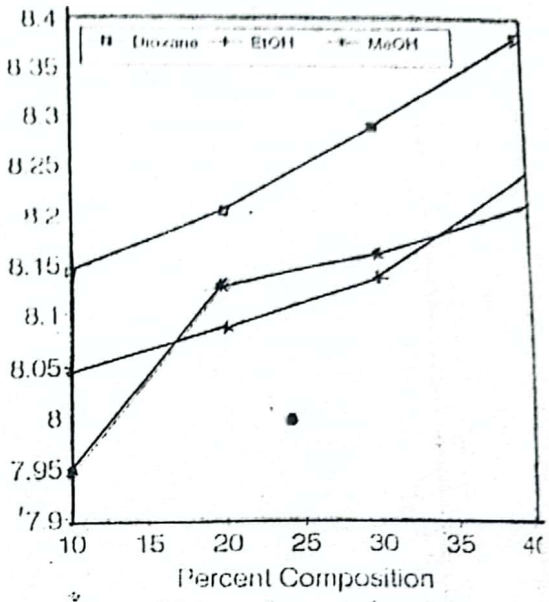


Fig.2 Effect of organic-water solvent mixture on pKb values of tris.

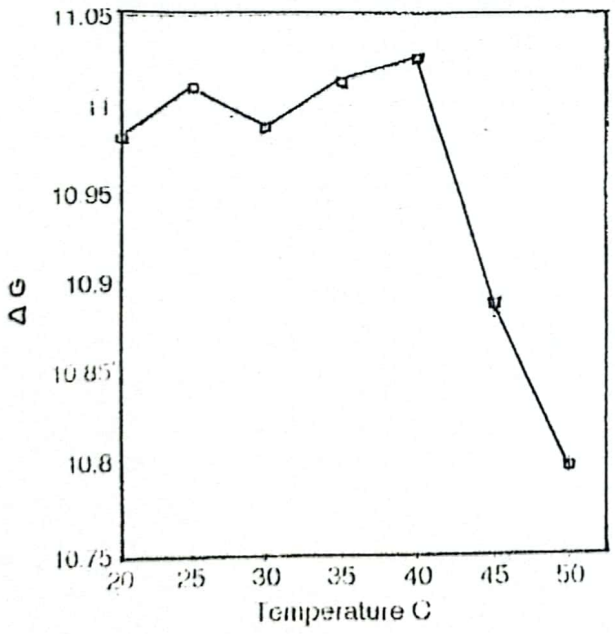


Fig.3 Effect of temperature on ΔG values of tris.

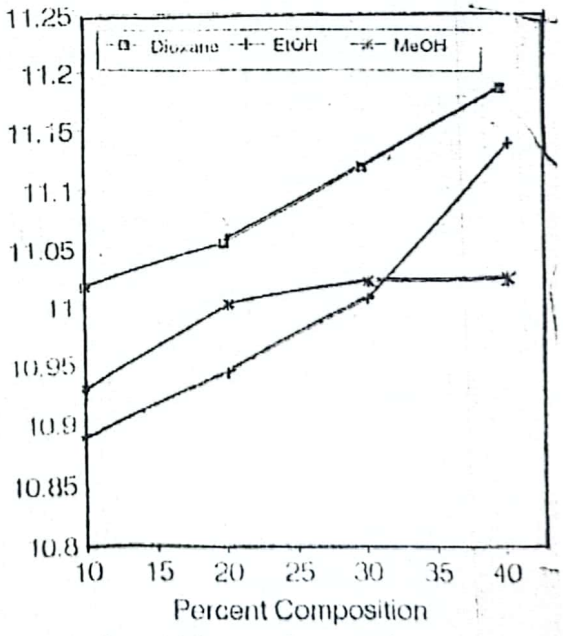


Fig.4. Effect of organic-water solvent mixture on ΔG values of tris.