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A COMPUTATIONAL METHOD FOR CALCULATION OF EQUILIBRIUM CONSTANT OF TARTARIC ACID AT DIFFERENT TEMPERATURE AND IN DIOXANE-WATER SOLVENT SYSTEM

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Abstract

Thermodynamic dissociation constants study of Tartaric acid has been carried out in aqueous media at different temperature 20, 25, 30, 35, 40, 45 and 50°.C and in 10, 20, 30, 40 percent v/v dioxane-water solvent system at 25°C potentiometrically. The influence of solvent composition and temperature on ionic equilibria has been studied. The computer program is written in GW-BASIC which is changed version of FORTRAN IV, has been modified and developed to be used with IBM PC< XT/AT or compatible computers. This program can be used to improve numberical relaibility, memory and computing time.

Introduction

This paper is a part of our research on dissociation constant [1,2]. The pH titration methods for the determination of dissociation constants of weak acids and bases are accurate and less time consuming as compared with other methods such as conductometric and spectrophotometeric methods [3-6].

The potentiometric methods therefore are being widely used to investigate the ionic equilibria in equeous and non aqueous solvents [3,7,8]. The dissociation constants of weak acids and bases are the constants which reveal the proportions of different ionic species present in the solution at a particular temperature and it is the indication of strength of that acid or base [3]. The dissociation constants are temperature and solvent concentration dependent [3,9]. The ionic speices differ in physical and biological properties, therefore it is very important to have a knowledge of dissociation constants of biological substances in spectrocopy and in preparative chemistry [10]. The dissociation constants also reveal structure of newly isolated species [11]. It has been observed from literature that the temperature and solvent

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dependant pK_a values of biologically important substances are not often available [10,12,14]. The pH-titration methods have been refined by using micro titration unit, purified and dried nitrogen gas, carbon dioxide free alkalic, standardized glass electrode, precision pH meter, temperature control accurate to ± 0.1 and availability of computer programs for calculation of accurate pK_a values from experimental data [3,8,15-17].

The problem of accuracy arises for the determination of two pK_a values where the difference due to overlapping is 2.7 units or less in ionization proceses. Speakman derived an equation which allows to calculate two overlapping pKa values accurately [18]. The computer program written in GW-BASIC which is a changed version of FORTRAN IV, and has been modified and developed to be used with IBM PC XT/AT or compatible computers [3,19]. The object to undertake this work was firstly to acheive an accurate, reproducible and reliable results by observing refined and improved techniques, secondly to investigate an aqueous and non aqueous solvent and temperature effect on pK_a values [12,20,21].

Theory for Overlapping Ionization Processes

When polybasic substances are titrated, it is observed that the pK_a values are of poor precision because the end point of the first equivalence point is indefinite and titration of one group began before the other is completed. When this occurs, the two ionization processes are said to be overlapping.

Speakman [16] derived an equation which allows these pK_a values to be calculated. It can be written in the form of

$$\frac{1}{K_1^M} \cdot \frac{(a_H+)2 \cdot F}{(2 - F)} - K_2^M = (a_H+) \cdot \frac{(1 - F)}{(2 - F)} \qquad (1)$$

where

$$F = \frac{(CA + a_H+ - A_{OH}-1)}{C} \qquad (2)$$

where K_1^M amd K_2M are concentation constants, a is activity. C and CA are as follows

$$C = \frac{W \cdot 1000}{M\ (V + V_t)} \quad ; \quad CA = \frac{V_t \cdot N}{(V + V_t)} \qquad (3)$$

Where W is weight and M is molecular weight of acid taken, V is volume of water in which acid is dissolved and V_t is volume of NaOH to be added as titrant.

The ionization processes for a dibasic acid can be represented as

$$H_2A \text{ ----------- } H^+ + HA^{-1} \quad ; \quad HA^{-1} \text{ ------------ } H^+ + A^{-2} \qquad (4)$$

$$K_1^T = K_1^M \cdot f_{HA^-} \text{ and } K_2^T = K_2^M \cdot \frac{f_{A^{2-}}}{f_{HA^-}} \qquad (5)$$

Where K_1^T and K_2^T are thermodynamic dissociation constants and f are activity coefficients.

If we define

$$FS = \frac{(I)^{0.5}}{[1 + 1.5(I)^{0.5}]} \text{ and } f_i = \frac{1}{10^{AZ^2 FS}} \qquad (6)$$

Where $I = 0.5 \; \Sigma \; Ci \; Z^2$, Ci is molar concentration, Z is valency of ion and A is constant. At 25°C Eq(5) becomes

$$K_1^T = K_1^M \; / \; 10^{(0.5115 \; . \; FS)} \qquad (7)$$

$$K_2^T = K_2^M \; / \; 10^{(1.5345 \; . \; FS)} \qquad (8)$$

Eq (1) now becomes

$$\frac{1}{K_1^T} \; \frac{(a_H +)2 \; , \; F \quad 1}{(2\text{-}F) \quad 10^{(0.5115.FS)}} - K_2^T \; . \; 10^{(1.5345.FS)} = (a_H+). \; \frac{1 - F}{(2 \; \text{-}F)} \qquad \text{--------}(9)$$

On rearranging Eq(9) we get

$$\frac{1}{K_1^T} \; \frac{X}{10(^{2.046.FS)}} - K_2^T = \frac{Y}{10(^{1.5345. \; FS)}} \qquad (10)$$

or

Eq (1) and Eq (10) are used to calculate K_1T and K_2T by method of least squares.

Experimental

All the reagents were of analytical grade and were used without further purification. Fresh, purified and distilled 1,4-Dioxane was used. All the solutions were prepared in doubly distilled and carbon dioxde free conductivity water, tartaric acid solution of 0.00978M in 0.005M. HC1 was prepared. sodium hydroxide solutions of 0.1 M in water and in 10,20,30, and 40 % v/v dioxane-water were also prepared and standardized against potassium hydrogen phthalate dried at 120°C by potentiometric method. The potentiometric titration was performed in thermostated jacket cell containing Ingold combined glass and Ag/Agcl reference electrode saturated with potassium chloride. The temperature of the cell was kept constant by circulating water from JULABO HC thermostated bath accurate to ± 0.1°C. Prior to pH-metric experiments the glass electrode was calibrated with 0.05 M potassium hydrogen phthalate ($pH_{25^\circ C}$ = 4. 008) and 0.01 M $Na_2B_4O_7 \cdot 10H_2O$ ($pH_{25^\circ C}$ = 9.18).

The pH of titrand in the cell was measured with PHILIPS PW 9420 digital pH-meter. The titrant was delivered by Mettler DV 210 dispenser readable to ± 0.01 ml. The potentiometric titrations were performed on 50 ml Tartaric acid as titrand and sodium hydroxide as titrant. The solution was mixed by means of magnetic stirring and was made carbonic acid free by bubbling a purified nitrogen gas. The experimental data were collected under different conditions of temperature and composition of solvent. The pK_a values of tartaric acid were calculated from the mean of three experimental data by Computer programme in GW-BASIC.

Results and Discussions

Results summerize in Table 1 is a computer out put when 50 ml of 0.00978 M tartaric acid solution was titrated with 0.1 M sodium hydroxide.

From Table 1 it is observed that pK_a values of tartaric acid are effected with change in the temperature but not in a systematic manner. Fig. 1 further shows that pK_1 values show slight decrease from 25°C to 40°C and increase after 45°C while pK_2 values decrease from 20°C to 30°C then increase from 35°C to 50°C.

The behaviour of pK_1 and pK_2 values of tartaric acid with temperature change is usually parabolic. The pK_1 shows a minimum around 40°C while pK_2 shows a minimum around 30°C. The pK_n values are temperatur sensitive. In previously reported literature [20] perhaps temperature control bath was not better that is why the values are not consistent. In the present case, the bath temperature is very accurate ± 0.1°C. This is the reason a better minimum is observed in present case.

Non-aqueous acid base titration finds many application in the analysis of organic and ingroganic substances [24]. Mixture of water with organic solvents, particularly dioxane is popular media for studing acid behaviour.

Table 2 shows a systematic increase in pK_1 and pK_2 values of tartaric acid at 25°C with increase in concentration of dioxane-water solvent. Fig. 2 further elaborate the effect of solvent.

This behaviour of pK_n values of tartaric acid with increase concentration of solvent may be due to increaseing the ionic association. The pK_n values pK_n of tartaric acid are comparable and are in good agreement with the reported pK_n values of tartaric acid. Further work is in progress to study the influence of temperature and concentraction of other organic solvents on the pK_n values of other biologically important substances.

It is concluded that both temperature and concentation of solvent has notable effect on pK_a values.

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Table-1

Substance = Tartaric acid
Molecular Weight = 150.09
0.0734 G Dissolved in 50 ML of Water
Containing 50 ML of 0.005 M HCL = 0.00978M
Molarity of Titrant = 0.1 M Temperature = 25 °C

Vol	PH	X	Y	I	PK1	PK2
1.000	2.760	0.57309E-06	0.53284E-03	0.39521E-02	3.001	
1.400	2.840	0.45514E-06	0.41427E-03	0.4475E-02	3.001	
1.800	2.920	0.36179E-06	0.31754E-03	0.49837E-02	2.997	
2.200	3.010	0.27245E-06	0.23445E-03	0.55870E-02	3.006	
2.600	3.090	0.21636E-06	0.17231E-03	0.61972E-02	2.996	
3.000	3.180	0.16299E-06	0.12002E-03	0.68779E-02	2.997	
3.400	3.270	0.12280E-06	0.79307E-04	0.75959E-02	2.995	
3.800	3.360	0.92536E-07	0.47790E-04	0.83498E-02	2.987	
4.200	3.460	0.66438E-07	0.23175E-04	0.91956E-02	2.992	
5.800	3.760	0.29451E-07	-.32658E-04	0.12279E-01		4.486
6.200	3.930	0.15422E-07	-.32570E-04	0.13832E-01		4.487
6.600	4.070	0.94428E-08	-.33246E-04	0.15216E-01		4.478
7.000	4.210	0.58713E-08	-.33017E-04	0.16605E-01		4.481
7.400	4.350	0.37269E-08	-.32516E-04	0.17948E-01		4.488
7.800	4.480	0.25524E-08	-.33061E-04	0.19127E-01		4.481
8.200	4.630	0.16589E-08	-.32891E-04	0.20318E-01		4.483
8.600	4.800	0.10599E-08	-.32971E-04	0.21441E-01		4.482

AVERAGE PK_1 = 2.997 PK_2 = 4.483

Table-2

Themodynamic pK_n values of Tartaric Acid in Water at Various Temperature

Temperature	pK_n Evaluated		pK_n Reported	
°C	n=1	n=2	n=1	n=2
25	3.006 ± 0.003	4.484 ± 0.003	3.036	4.366
30	2.952 ± 0.008	4.474 ± 0.002		
35	2.900 ± 0.005	4.482 ± 0.005		
40	2.887 ± 0.004	4.493 ± 0.005		
45	2.921 ± 0.006	4.517 ± 0.004		
50	2.943 ± 0.004	4.532 ± 0.004		

Table-3

Thermodynamic pK_n values of Tartaric Acid in various Dixoxane-Water solvent system at 25°C

Dioxane-Water	Evaluated pK_n	
% v/v	n=1	n=2
10	3.571 ± 0.004	4.616 ± 0.001
20	3.803 ± 0.004	4.814 ± 0.003
30	4.153 ± 0.004	5.114 ± 0.003
40	4.360 ± 0.004	5.541 ± 0.004

Fig-1

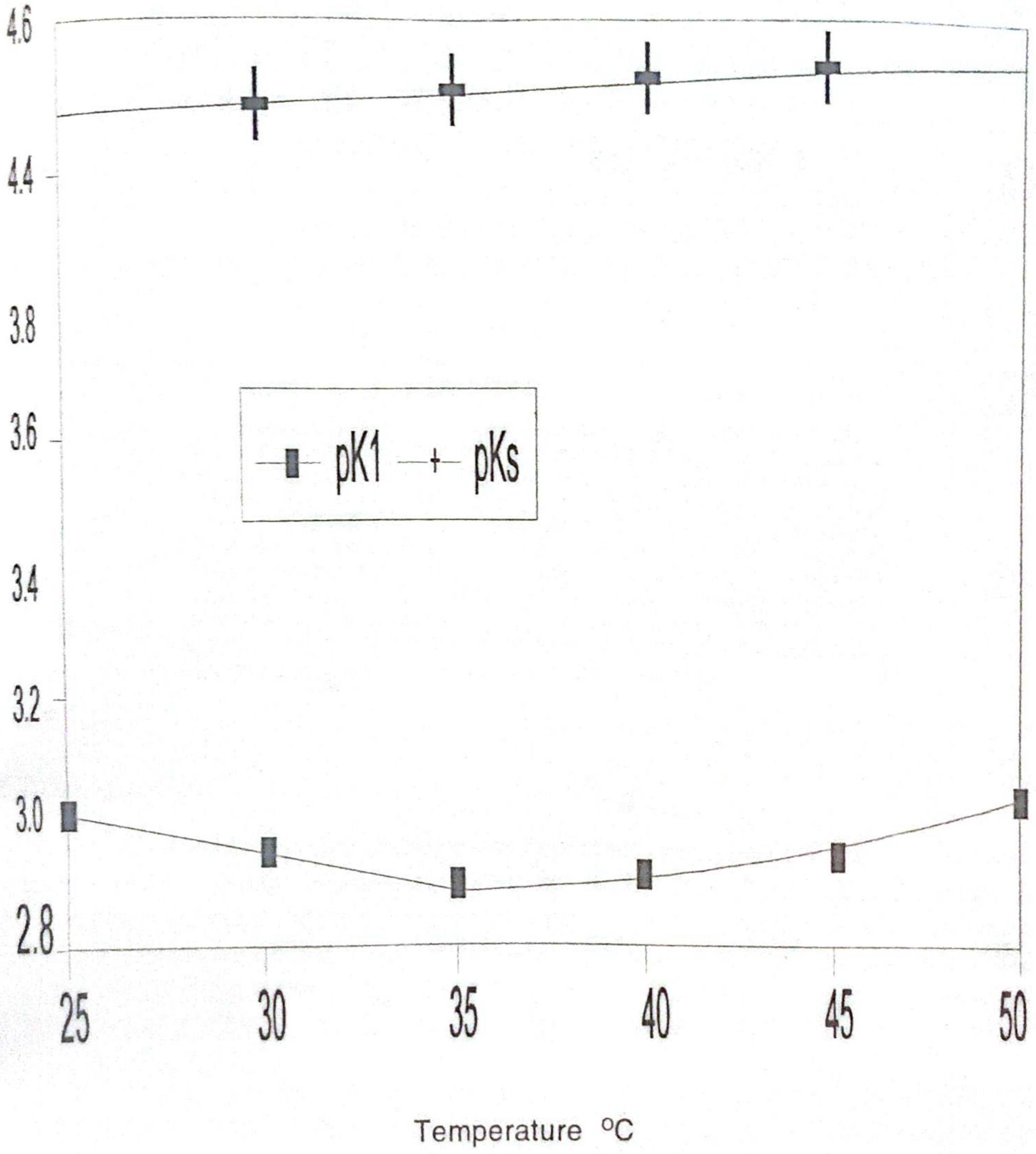
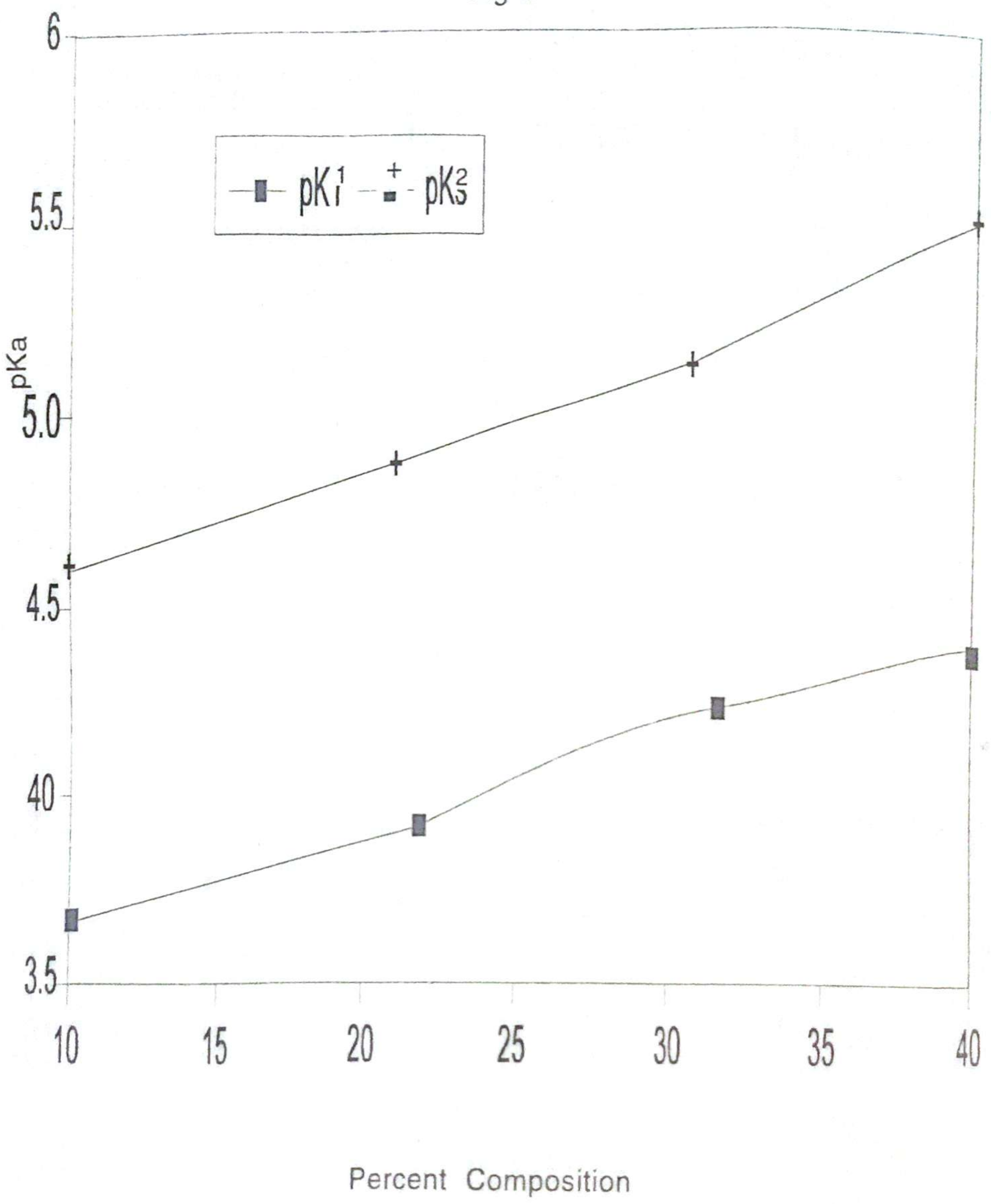


Fig-2


6
5.5
5.0
4.5
40
3.5
pKa
pKi1
pKs2
10
15
20
25
30
35
40
Percent Composition