

Acid-base Equilibria of Succinic and Tartaric Acid in Binary Organic – water Solvent Systems

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Summary: Ionization constants of two overlapping dibasic acids, succinic acid (butandioic acid) and tartaric acid (2,3-dihydroxybutandioic acid) have been studied at different temperatures between 25 to 50°C and in mixed organic-water solvent mixtures (dioxane-water, ethanol-water and methanol-water). Both succinic and tartaric acids are symmetrical dicarboxylic acids with the same length of carbon chain but are markedly different in ionic behaviour at different temperatures and in all solvent systems. The effect of temperature on the thermodynamic parameters were calculated and interpreted.

Introduction

This paper is a part of our research on ionization constants [1-4]. The pH titration method for the determination of ionization constants of weak acids and bases are accurate and less time consuming as compared with other methods [5-8].

The potentiometric method therefore are being widely used to investigate the ionic equilibria in aqueous and non aqueous solvents [5,9-11].

When polybasic substances are titrated, it is observed that the pKa 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 process is said to be overlapping. The problem of accuracy arises for the determination of two pKa values (pK₁ and pK₂) where the difference due to overlapping is 2.7 or less in ionization.

Speakman [12] derived an equation which allows to calculate two pK_n values accurately. 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 IBN-PC XT/AT computers [5,11,13].

The object to undertake this work was to see the effect of temperature and mixed solvent systems on pK_n values of two different organic acids (succinic and tartaric). Also to study the effect of

changing temperature on the calculated thermodynamic functions.

Results and Discussion

Table-1 list the pK_n values for succinic and tartaric acids at different temperatures. A glance at the same table indicates that pK₁ and pK₂ values are affected with change in temperature but not in a systematic manner.

Table –1: Effect of Temperature on pK_n Values of Succinic Acid and Tartaric Acid in Aqueous Media

| Temp. °C | Succinic Acid | | Tartaric Acid | |
|-------------|-----------------|-----------------|-----------------|-----------------|
| | pK ₁ | pK ₂ | pK ₁ | pK ₂ |
| 25 | 4.203 ± 0.007 | 5.723 ± 0.02 | 3.006 ± 0.003 | 4.484 ± 0.011 |
| 30 | 4.186 ± 0.008 | 5.701 ± 0.03 | 2.953 ± 0.008 | 4.474 ± 0.022 |
| 35 | 4.138 ± 0.003 | 5.686 ± 0.03 | 2.900 ± 0.005 | 4.484 ± 0.009 |
| 40 | 4.053 ± 0.005 | 5.652 ± 0.02 | 2.887 ± 0.006 | 4.493 ± 0.013 |
| 45 | 3.921 ± 0.002 | 5.543 ± 0.03 | 2.921 ± 0.006 | 4.517 ± 0.015 |
| 50 | 3.770 ± 0.002 | 5.445 ± 0.01 | 2.943 ± 0.004 | 4.532 ± 0.009 |

Inspection of (Table-1) shows that pK₁ and pK₂ values for succinic acid decreases gradually when temperature increases from 25 to 50°C. It was found that pK₁ values decreases from 4.203 and 3.770 and pK₂ values from 5.723 to 5.445 and total loss observed are 0.433 and 0.278 unit for pK₁ and pK₂ respectively. While in case of tartaric acid pK₁ values decreases gradually when temperature increases from 25 to 40°C then began to increase parallel to temperature upto 50°C.

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It can be also seen from the same table that pK_2 values for tartaric acid are decrease as in case of succinic acid from 4.484 to 4.474 when temperature increases from 25 to 30°C, further increase in temperature upto 50°C showing slight increase in pK_2 values. This behaviour is markedly different than succinic acid for the same range of temperature. This abrupt behaviour of tartaric acid may be attributed to the existance of two extra hydroxyl groups which affect the rate of ionization of tartaric acid in its media.

Actually when an electrolyte is dissolved in solvent (aqueous or non-aqueous) then dissociation of solute is not independent, few forces play an important role i.e. nature of electrolyte (strong or weak), hydrogen bonding, dielectric constant of solvent which varies with change in temperature, polarity of solvent in which electrolyte is dissolved and ionic size etc. Change in pK_a values of particular compound is a result of all these effects which bring structural change in compound which in turn effect on ionization of substance as a result pK_n values change.

Mixture of water with organic solvents particularly alcohols and dioxane are popular media for studying acid behaviour [17]. In the present case we used dioxane, ethanol and methanol solvents. Organic compounds that are not soluble in water are often brought into solution by addition of organic solvents. Organic solvents may be used as mixture with that of water. One of the most important property of a solvent is its dielectric constant, which difine to a considerable degree of solvating ability of the medium.

Solvent may be distinguished according to their dielectric sontant values and also their tendency to form hydrogen bonds. Both these properties took into consideration and in selecting the above solvents (dioxane, ethanol and methanol). The selection based on the fact that water, ethanol and methanol are the solvents having dielectric constant values 78.5, 24.3 and 32.6 respectively at 25°C and also having ability to form hydrogen bonds while dioxane = 2.21 but has no ability to form hydrogen bond.

Fig. 1a shows that by increasing the composition of organic solvents (dioxane, ethanol and methanol) in the mixtures, pK_1 values for succinic acid increases. This figure also shows that as

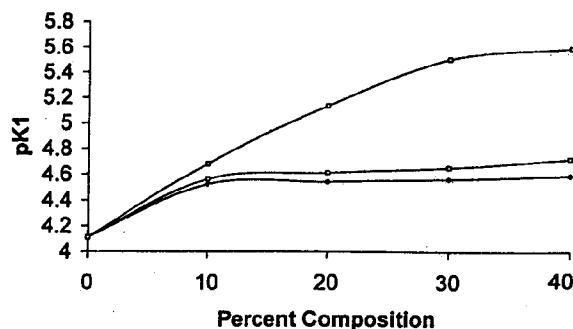


Fig. 1a: Effect of different composition of organic-water solvent mixture on pK_1 values of succinic acid at 25°C.

composition changes from 0 (only aqueous) to 10% (mixture of organic solvents-water) then no sharp increase in pK_1 values has been marked. It is also clear that total increase in pK_1 values are 1.610, 0.659 and 0.609 for dioxane-water, ethanol-water and methanol-water solvent systems respectively when composition of organic solvent increases from 0 to 40%.

Fig. 1b showing the effect of solvents mixture on pK_1 values of tartaric acid at 25°C. This figure clearly indicates that as composition of organic solvent increases from 0 to 10% then increase in pK_1 values is significant as compare to succinic acid, but there is no sizable increase in pK_1 values when composition of organic solvent increase from 10 to 40%. Total increase in pK_1 values in dioxane-water solvent mixture is much higher than in ethanol-water and methanol-water for both succinic and tartaric acids. Possible reason is that the dielectric constant value of dioxane is 2.21 while for ethanol and methanol are 32.6 and 24.3 at 25 C. We know that lower the values for dielectric constant, higher will be the pK values [18]. pK values in ethanol-water and methanol-water are close as compare to in dioxane-water, actually dielectric constant values of methanol and ethanol are close (32.6 and 24.3 at 25°C) so the pK values are also close.

Comparision of Fig. 1a and Fig. 1b also indicates that total increase in pK_1 values at 25°C are much higher for tartaric acid as compare to succinic acid, because when composition of organic solvents increase from 0 to 40% then total increase in pK_1 values for succinic acid are 1.610, 0.659 and 0.609 in dioxane-water, ethanol-water and methanol-water

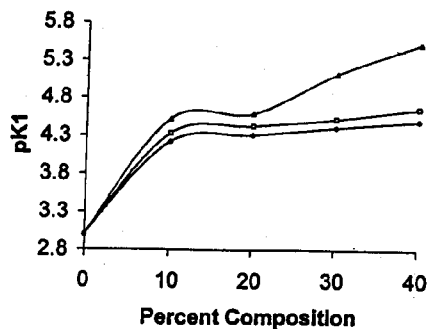


Fig. 1b: Effect of different composition of organic-water solvent mixture on pK_1 values of tartaric acid at 25°C

while for tartaric acid 2.559, 1.650 and 1.530 in the same solvent mixtures respectively.

Fig. 2a and Fig. 2b showing the effect of nature of solvents and their different composition on pK_2 values for succinic acid tartaric acid respectively. These figures again repeating the same pattern as in Fig. 1a and 1b. It is clear that as composition of organic solvents (dioxane, ethanol and methanol) increases then pK_2 values for both acids also increases but not linearly. These figures again showing that values in methanol-water and ethanol-water are close as compare to in dioxane-water solvents systems.

Table-2 shows the effect of temperature on thermodynamic constants (ΔG , ΔH , ΔS) for succinic and tartaric acids. Change in thermodynamic functions can be calculated by using equation (1) [16].

Table-2: Effect of Temperature on Thermodynamic Constants of Overlapping Dibasic Acids in Aqueous Media.

| Organic Compound | Temp. $^\circ\text{C}$ | ΔG KJ/mol | | ΔH KJ/mol | | ΔS KJ/mol | |
|------------------|------------------------|-------------------|--------------|-------------------|--------------|-------------------|----------------|
| | | ΔG_1 | ΔG_2 | ΔH_1 | ΔH_2 | ΔS_1 | ΔS_2 |
| Succinic Acid | 25 | 23.991±0.009 | 32.664±0.01 | 8.883±0.007 | -5.640±0.003 | -50.656±0.01 | -128.482±0.006 |
| | 30 | 24.292±0.003 | 33.083±0.008 | 8.933 ± 0.005 | -5.866±0.01 | | |
| | 35 | 24.527±0.007 | 33.865±0.004 | 8.916±0.01 | -5.724±0.01 | | |
| | 40 | 24.711±0.008 | 34.547±0.005 | 8.845±0.01 | -5.602±0.009 | | |
| | 45 | 24.991±0.01 | 35.275±0.008 | 8.870±0.008 | -5.686±0.01 | | |
| Tartaric Acid | 25 | 17.104±0.008 | 25.585±0.006 | 4.732±0.005 | -3.870±0.008 | -41.484±0.01 | -98.809±0.009 |
| | 30 | 17.083±0.006 | 25.966±0.009 | 4.506±0.003 | -3.987±0.007 | | |
| | 35 | 17.058±8.008 | 26.439±0.009 | 4.272±0.005 | -4.008±0.007 | | |
| | 40 | 17.259±0.009 | 26.928±0.01 | 4.263±9.01 | -4.012±0.008 | | |
| | 45 | 17.748±0.01 | 27.509±0.008 | 4.548±0.009 | -3.924±0.01 | | |
| | 50 | 18.154±0.01 | 28.029±0.01 | 4.749±0.02 | -3.899±0.01 | | |

$$pK = \frac{\Delta H}{RT} - \frac{\Delta C_p}{R} \ln T - \frac{\Delta S}{R} + \frac{\Delta C_p}{R}$$

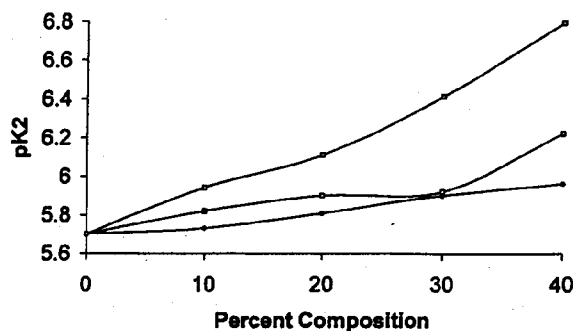


Fig. 2a: Effect of different composition of organic-water solvent mixture on pK_2 values of succinic acid at 25°C .

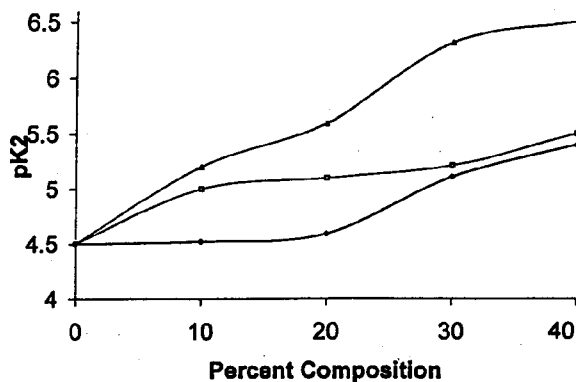


Fig. 2a: Effect of different composition of organic-water solvent mixture on pK_2 values of tartaric acid at 25°C

If C_p is zero over temperature range investigated then above equation can be reduced as

$$pK = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$$

Where ΔH and ΔS are the molar enthalpy and entropy change of acid-base equilibria in their solvents.

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

Where ΔG is the molar free energy change.

This data leads us to conclude that the pK_n values for tartaric acid are higher as compare to succinic acid for same solvent mixtures although both dicarboxylic acids have same length of carbon chain. We also found that pK_n values are different in different solvents because each solvent has its own dielectric constant value, hence we can say that both temperature and solvent's nature have notable effect on ionization constant.

Experimental

Reagent grade succinic and tartaric acid (Merck) used were dried in vacume for overnight. The purity of acids were checked by potentiometric titration 0.01 M solution of succinic and tartaric acid each were prepared by direct weighing and dissolution in 50 ml water just before use. The titrant 0.1 M sodium hydroxide solution (carbonate free standaerized with potassium hydrogen phthalate) was prepared in water and also in mixed solvents (dioxane-water, ethanol-water, methanol-water).

Double distilled deionized conductivity water ($1.0 \times 10^{-6} \text{ S cm}^{-1}$ at 25°C) was used throughout the experiment. Dioxane, methanol and ethanol used in this study were also purified [14].

Prior to experiment pH meter was calibrated with know buffer of potassium hydrogen tartarate ($\text{pH } 25^\circ\text{C} = 3.557$), potassium hydrogen phthalate ($\text{pH } 25^\circ\text{C} = 4.005$) and dihydrogen phosphate ($\text{pH } 25^\circ\text{C} = 6.865$) [5,15] in respective solvents.

The potentiometric titration were performed in thermostated jacket cell containing ingold combined glass and Ag/AgCl reference electrode saturated with potassium chloride. The temperature of the cell kept

constant by circulating water from JULABO HC thermostated bath with accuracy $\pm 0.1^\circ\text{C}$.

The pH of titrant in the cell was measured with PHILLIPS PW 9420 digital pH-Meter. The titrant was delivered by Mettler DV-10 dispenser readable to 0.01 ml.

Before and during measurement, sample solution was kept at inert atmosphere by bubbling purified nitrogen gas [5].

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