

Dissociation Constant Studies of Lactic Acid at Different Temperatures and in Mixed organic – water Solvent Systems

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Summary: Dissociation constants of lactic acid (2-hydroxy propionic acid) have been studied at different temperatures between 25 to 50°C interval in aqueous media and in mixed organic-water solvent systems (dioxane-water, ethanol-water and methanol-water) at 25°C. Potentiometric data was analysed for calculation of pK_a values of monobasic acids. Results shows that pK_a values are higher in mixed solvents as compare to in aqueous media. Significant effect of temperature and solvent's nature on pK_a values has been observed.

Introduction

Heart muscle is especially capable of converting lactic acid to pyruvic acid and then utilizing it for energy. This occurs to a great extent in every heavy exercise, during which large amount of lactic acid are released into the blood from the skeletal muscles and then are consumed as an extra source by the heart [1].

Dissociation constant 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 acids and bases [2].

The ionic species of same substance may differ in physical, chemical and biological properties, therefore it is very important to have a knowledge of dissociation constants of biological substances [3]. Dissociation constant also reveal the structure of newly isolated species [4].

Survey of literature shows that much data on effect of temperature and solvent's nature on pK_a values is not available frequently. Actually lengthy and time consuming exercise to calculate the dissociation constants was main obstacle in a way. We developed computer program in GW-BASIC to overcome this problem, program can be used to improve numerical reliability and computing time.

Several methods have been reported for the determination of pK_a values, these are potentiometry [5-9], conductometry [10-11], spectrophotometry

[12-15] and high performance liquid chromatography [16,17]. Among all potentiometric method is widely used to determine pK_a values because it is less time consuming as compare to other methods and procedure results with high accuracy.

The aim of present work is twofold, Firstly to study the effect of temperature and secondly the effect of solvent's nature on equilibrium constants of lactic acid.

Results and Discussion

The dissociation constants of lactic acid were determined in aqueous media at 25, 30, 35, 40, 45 and 50°C and in 10, 20, 30 and 40% organic-water solvent mixture at 25°C. A typical experiment performed is shown in Table 1. This computer output listed concentration ionization constant (pK_a^C), thermodynamic ionization constant (pK_a^T), percentage of ionization of sample at different pH, average values of pK_a^C and pK_a^T with standard deviation and also the Gibb's free energy (ΔG). Such type of computer output were obtained in triplicate at each temperature to get pK_a values. Reported pK_a values in this work are the average of three sets of experiments.

Table 2 shows the effect of temperature on pK_a values and thermodynamic parameters (ΔG, ΔH and ΔS). A change in temperature causes a shift in equilibrium point which is of practical and theoretical interest [20]. In this table pK_a values evaluated at 25°C close to reported results [2].

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Table-1:

Substance = Lactic acid
 Molecular weight = 90.08
 0.1802 gm Dissolved in 50 ml of Water
 Concentration of Acid = CS = 4.000888E-02 M
 Concentration of Alkalle = CA = 0.1 M
 Temperature = 25 Degree Celcius

Vol.	pH	HA	A	Log (HA/A)	% ion	pKa ^C	pKa ^T
1.00	2.85	0.036	0.003	1.026	8.118	3.876	3.904
2.00	3.03	0.034	0.005	0.848	11.642	3.878	3.910
3.00	3.17	0.031	0.006	0.695	15.649	3.865	3.902
4.00	3.30	0.029	0.008	0.566	19.836	3.866	3.907
5.00	3.42	0.027	0.009	0.453	24.157	3.873	3.917
6.00	3.52	0.025	0.011	0.351	28.05	3.871	3.917
7.00	3.61	0.023	0.013	0.256	33.140	3.866	3.915
8.00	3.71	0.021	0.014	0.166	37.734	3.876	3.928
9.00	3.79	0.018	0.015	0.079	42.427	3.869	3.923
10.0	3.88	0.017	0.017	-0.007	47.186	3.873	3.929
10.1	3.89	0.016	0.017	-0.015	47.665	3.875	3.931
10.2	3.91	0.016	0.017	-0.024	48.137	3.886	3.942

Average pKa^C = 3.873 ± 0.006

Average pKa^T = 3.919 ± 0.812

Gibb's free energy of pKa^T = 5.345 kcal/mole

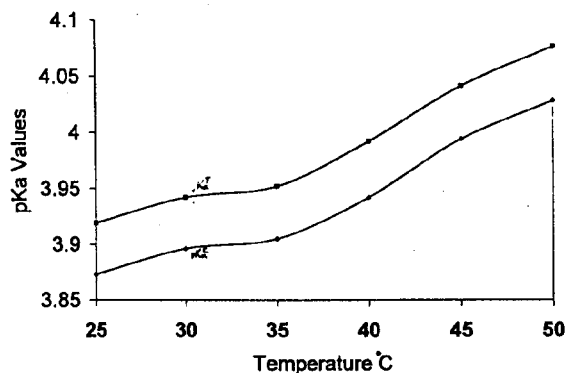


Fig.1: Effect of temperature on pKa values of lactic acid.

A closer inspection of Table 2 and Fig. 1 shows that there is minimum increase in pKa values (0.009 unit) when temperature increases from 30 to 35°C while there is maximum increase in pKa values (0.054 unit) between 40°C to 45°C.

Actually when an electrolyte dissolved in solvent (aqueous or non-aqueous) then dissociation of solute is not independent, few forces play an important role viz., 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

Table-2: Effect of Temperature on pKa Values and Thermodynamic Parameters of Lactic Acid in Aqueous Media

Temp. C	pKa value pKa ^c	Evaluated pKa ^T	PKa values reported	ΔG KJ/mol	ΔG KJ/mol
25	3.873±0.006	3.919±0.01	3.86*	22.363	-11.627
30	3.896±0.009	3.942±0.008		22.681	-11.686
35	3.905±0.006	3.942±0.008		23.309	-11.820
40	3.942±0.008	3.992±0.006		23.932	-11.811
45	3.994±0.01	4.041±0.007		24.610	-11.665
50	4.028±0.009	4.076±0.006		25.217	-11.632

Reference* [2]

and ionic size etc. Change in pKn 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 pKn values change.

Fig. 2 shows the effect of temperature on Gibb's free energy (ΔG). Increase in ΔG values has been marked with increase in temperature. Change in thermodynamic constants (ΔG, ΔH, ΔS) have been calculated by using equation (1)[20]

$$\Delta G = -RT \ln K$$

$$\text{Or } \Delta G = 2.303 RT \text{ pKa}$$

$$\text{pK} = \frac{\Delta H}{RT} - \frac{\Delta Cp}{R} \ln T - \frac{\Delta S}{R} + \frac{Cp}{R} \quad (1)$$

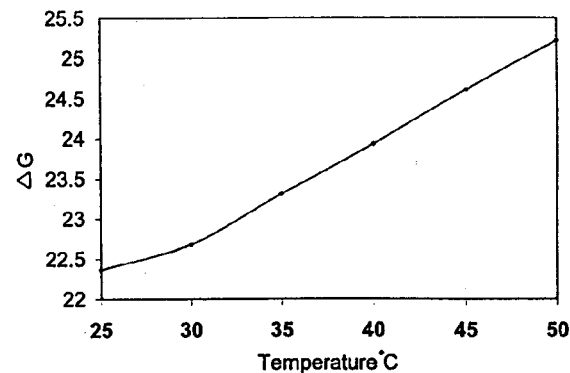


Fig.2: Effect of temperature on ΔG values of lactic acid.

If Cp is Zero over temperature range investigated the above equation can be reduces as

$$\text{pK} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad \text{-----} \quad (2)$$

Table-3: Showing the Effect of Temperature on pH and Percentage of Ionization of Sample

Vol. of NaOH in ml	25°C		30°C		35°C		40°C		45°C		50°C	
	pH	% Ion	pH	% Ion	pH	% Ion	pH	% Ion	pH	% Ion	pH	% Ion
1.00	2.85	8.118	2.87	7.964	2.88	7.887	2.91	7.676	2.95	7.417	3.99	7158
2.00	3.03	11.642	3.05	11.535	3.06	11.480	3.09	11.334	3.14	11.116	3.19	10.898
3.00	3.17	15.649	3.20	15.530	3.21	15.485	3.24	15.375	3.29	15.212	3.33	15.048
4.00	3.30	19.836	3.33	19.740	3.33	19.727	3.37	19.611	3.42	19.842	3.47	19.355
5.00	3.42	24.157	3.34	24.098	3.45	24.060	3.48	23.983	3.53	23.873	3.59	23.767
6.00	3.52	28.605	3.54	28.551	3.55	28.513	3.58	28.444	3.63	28.348	3.68	28.250
7.00	3.61	33.140	3.63	33.098	3.64	33.052	3.68	32.975	3.73	32.889	3.77	32.805
8.00	3.71	37.734	3.72	37.698	3.73	37.660	3.76	37.600	3.82	37.510	3.87	37.422
9.00	3.79	42.427	3.82	42.370	3.82	42.342	3.85	42.286	3.90	42.212	3.94	42.135
10.00	3.88	47.186	3.90	47.141	3.92	47.095	3.94	47.050	3.99	46.981	4.04	46.914
10.20	3.91	48.135	3.92	48.102	3.93	48.064	3.96	48.011	4.02	47.937	4.07	47.866

$$\text{Where } \Delta G = \Delta H - T \Delta S \text{ ----- (3)}$$

Actually change in thermodynamics constants ΔG , ΔH , ΔS associated with a acid-base reaction can be found from the variation of its equilibrium constant with temperature. These thermodynamic properties afford interesting insights into acid-base behaviour, particularly with regard to salvation effects.

Table 3 shows the effect of temperature on percentage of ionization of sample. As temperature increases, pH changes which in turn effect on percentage ionization of sample.

Percentage of ionization of sample is calculated by using equation (4) [2].

$$\% \text{ ionized} = \frac{100}{1 + 10^{(pK_a - pH)}} \text{ ----- (4)}$$

50 ml of 4×10^{-2} lactic acid solution was titrated with 0.1 M sodium hydroxide. Fig. 3 shows the effect of pH on percentage of ionization of sample. If we read Table.3 from left to right then we can see as temperature increases from 25°C to 50°C then pH of solution increases and percentage of ionization of sample decreases. If we go from top to bottom at each temperature then pH increases and percentage of ionization also increase.

In recent years non-aqueous 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. 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 defines to a considerable degree of the solvating ability of the medium [21].

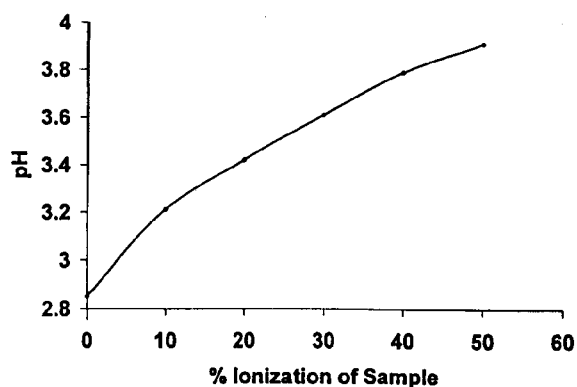


Fig.3: Effect of pH on percentage ionization of lactic acid.

There is considerable difference in the solvating ability of different solvents. In order to measure the effect of these mixed solvents (dioxane-water, ethanol-water and methanol-water) on pK_a values of lactic acid, an extensive investigation has been carried out.

Fig.4 and 5 shows the effect of solvent mixture on pK_a values and ΔG . These figures clearly indicate that as composition of organic solvents (dioxane, ethanol and methanol) increases in a mixture than pK_a values and ΔG values increases [18], but this increase is not constant between each 10% increment of organic solvents. It is noted from these figures that as composition of organic solvent increases from 10 to 20% then minimum increase in pK_a values has been marked while this increase is sizable between 30 to 40%. Difference in pK_a values in different solvent systems (dioxane-water, ethanol-water, & methanol-water) is because of difference in dielectric constant values which are 2.21, 24.3, and 32.6 for dioxane, ethanol and methanol respectively.

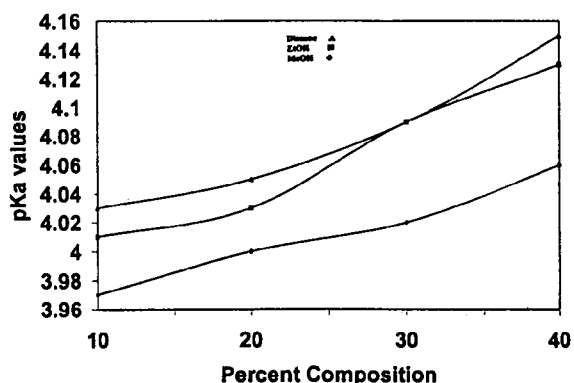


Fig.4: Effect of organic-water solvent mixture on pKa values of lactic acid.

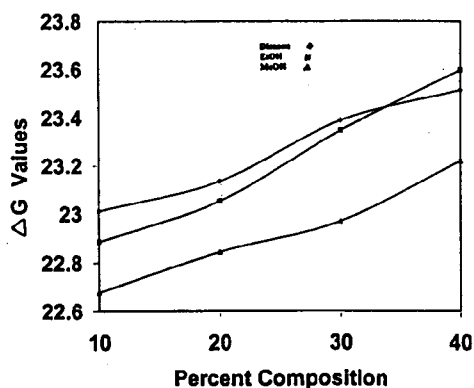


Fig.5: Effect of organic-water solvent mixture on ΔG values of lactic acid.

When composition of organic solvent increases in water then there is change in dielectric constant of medium because of solute solvent interaction. Beside this there is specific chemical interaction involve the destruction of one type of solvation shell and the creation of another (chemical or non electrostatic) factor. Thus, the change of dissociation constant of the acid for different percentage of solvent composition might be regarded as the sum of two terms firstly from Born relation and secondly obtained by subtracting the electrostatic term from the total pKa values.

After going through the experimental data we can conclude that temperature and solvent's nature has significant effect on pKa values for lactic acid.

Experimental

All chemicals were analytical grade and were used without further purification. Doubly degassed

distilled water was used in preparation of all solution. Fresh and distilled dioxane, ethanol and methanol were also used. Stock solution of 4×10^{-2} M lactic acid in water and 0.1M sodium hydroxide containing 10, 20, 30 and 40% dioxane, ethanol and methanol were also prepared. Sodium hydroxide solution was standardized with potassium hydrogen phthalate (dried at 120°C) by potentiometric method. The potentiometric titrations were performed in a thermostated double walled glass cell containing 50 ml of sample solution with sodium hydroxide. The pH was determined with PHILIPS PW 9420 digital pH meter which was coupled with Ingold combined glass and reference electrode dipped in sample solution whose temperature was controlled by circulating water through the jacket of measuring cell, JULABO HC thermostated bath accurate to $\pm 0.1^\circ\text{C}$ was used for controlling the temperature.

Prior to experiment the glass electrode was calibrated with 0.05 M potassium hydrogen phthalate (pH at $25^\circ\text{C} = 4.005$) and potassium dihydrogen phosphate and disodium hydrogen phosphate, each 0.025M (pH at $25^\circ\text{C} = 6.863$) in aqueous and in respective organic-water solvent mixture [2, 18]. Sample solution was kept mixed by stirring with magnetic stirrer and inert by bubbling nitrogen gas which was dried and purified by passing through Fieser's solution [2]. For dispensing titrant, Mettler burette DV-10 accurate to 0.01 ml was used.

The potentiometric measurement were performed on sample solution at different temperatures and in different solvents and their different compositions (10, 20, 30 and 40%). The potentiometric data was analyzed by a computer program written in GW-BASIC for calculation of dissociation constants of monobasic acids* (lactic acid).

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