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Determination of Dissociation Constants of Propionic Acid and Lactic Acid (2-hydroxypropionic acid) by Potentiometry and Conductometry

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Abstract

Dissociation constants of propionic acid and 2-hydroxypropionic acid (lactic acid) have been studied at different temperatures between 25 to 50 °C at 5°C interval. Propionic acid is analyzed by conductometry while 2-hydroxypropionic acid is analyzed by potentiometry. Both investigated compounds are symmetrical carboxylic acids having same length of carbon chain but are markedly different in ionic behaviour. We were interested to see how the hydroxyl group (-OH) induction in propionic acid affects on pKa values of 2-hydroxypropionic acid. We observed that as temperature increases pKa values increases. The increase is observed for both the investigated compounds. pKa values of 2-hydroxypropionic acid are lower as compared to propionic acid because of electron withdrawing group (-OH).

Introduction

The dissociation of weak acids and bases are the constants which reveal the proportion of different ionic species present in the solution at a particular temperature and it is the indication of strenth of that acid or base [1]. The dissociation constant are temperature and solvent concentration dependent. The ionic species differ in physical and biological properties, therefore it is very important to have a knowledge of dissociation constants of biological substances in spectroscopy and in preparative chemistry [2,3].

This paper is a part of our research on dissociation constants. The pH titration method for the determination of dissociation constants of weak acids and bases are accurate and less time consuming as compared to other methods such as conductometric and spectrophotometric methods [4-10].

A conductometric determination of pKa value differs particularly from the corresponding potentiometric determination in the way that the values in a set are obtained by simple dilution and not by titration with acid or alkali at a fixed concentration. Hence each conductometric reading may need different activity corrections and make the calculations lengthy and quite tedious [11-14]. Beside this the practical work is at least twice as time consuming as compared to potentiometry but a special advantage of conductiometry is that significant results can be obtained at great dilution.

In this work lactic acid (2-hydroxy propionic acid) is being analyzed by potentiometry while propionic acid is analyzed by conductometry.

We are interested to see the effect of temperature on pKa values for 2-hydroxy propionic acid and propionic acid. We also studied the effect of hydroxyl group induction in 2-hydroxy propionic acid. Both investigated acids have same length of carbon chain but markedly different in ionic behaviour because of the hydroxyl group(-OH).

Theory for Potentiometric Data

Any monobasic acid HA dissocitae as follows:-

$$HA \rightleftharpoons H^+ + A^- \tag{1}$$

$$K_a^C = \frac{[H^+][A^-]}{[HA]} \tag{2}$$

$$pK_a^C = pH + \log\frac{[HA]}{[A^-]} \tag{3}$$

Where the term in square bracket [ ] represent molar concentration. pK_a^C is concentration ionization constant. When titrating an acid with base, electric neutrality gives :

$$[A^-] + [OH^-] = [Na^+] + [H^+] \tag{4}$$

$$\text{or} \ [A^-] = [Na^+] - [OH^-] + [H^+] \tag{5}$$

If C_o is the total ion concentration of acid taken, then

$$C_o = [A^-] + [HA] \tag{6}$$

$$[HA] = C_o - [A^-] \tag{7}$$

Substituting the values of $[A^-]$ from Eq. (5) in Eq. (7) we get

$$[HA] = C_o - [Na^+] + [OH^-] - [H^+] \tag{8}$$

Eq. (2), (3) and (8) have been used to calculate pK_a^C values using no approximation.

The general formulation of the relationship between the concentration of an ion C_i and its acticity coefficient Y_i is based on the work of Debye-Hückel [2,3]. An important term in the formulation is the ionic strength, written as I and is defined as :

$$I = \frac{1}{2}\Sigma C_i z_i^2 \tag{9}$$

Where C_i is the molar concentration and z_i is the valency of ion respectively and Σ denotes summation over i. According to Debye-Hükel theory, the activity coefficient γ_i of an ion of valency z_i is related to the ionic strength I by :

$$-\log\gamma_i = \frac{Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} \tag{10}$$

The term A and B are Debye–Hückle constants which vary with the dielectric constant and temperature of the solvent [16]. The term ai is the ionic size parameter, that is the mean distance of approach of the ions, for which 4.5×10^{-10} m may be taken as an average value. The thermodynamic ionization or dissociation constants can be written as [10].

$$K_a^T = \frac{a_{H^+} . a_{A^-}}{a_{HA}}. \tag{11}$$

Where

$$a_{H^+} = pH, \ a_{A^-} = [A^-]\gamma_{A^-} \ \text{and} \ a_{HA} = [HA]\gamma_{HA} \tag{12}$$

In which the term γ_i activity coefficient calculated by means of Eq (10) and term a_i is the activity of respective ion.

Hence at a temperature of 20°C concentration ionization constant (pK_a^c) can be converted to thermodynamic ionization constant (pK_a^T) by using Eq. (11).

$$pK_a^T = pK_a^C + \frac{0.507\sqrt{I}}{1 + 1.5\sqrt{I}} \ \text{for acids} \tag{13}$$

Theory for Conductiometry

A weak acid dissociate according to Eq. (14)

$$HA \rightleftharpoons H^+ + A^- \tag{14}$$

$$K_a^C = \frac{[H^+][A^-]}{[HA]} \tag{15}$$

If the degree of dissociation is α, then $[H^+] = \alpha$, $[A^-] = C\alpha$ and $[HA] = C(1-\alpha)$ where terms in square bracket are molar concentration in moles/liters or mole/kg.

Eq. (15) can be written in term of α,

Table-1 Effect of Temperature on pKa Values & ΔG values of Propionic acid & 2-hydroxypropionic acid in aqueous media.

Organic Compound	Temperature C	pKa Values evaluated		pK_a^T Values reported*	ΔG kJ/mol
		pK_a^C	pK_a^T		
Propionic acid	25	4.842±0.01	4.855±0.01	4.874	27.706
	30	4.850±0.02	4.863±0.01		28.221
	35	4.860±0.01	4.873±0.02		28.744
	40	4.873±0.009	4.885±0.01		29.284
	45	4.884±0.02	4.897±0.01		29.824
	50	4.988±0.01	4.978±0.02		30.380
2-hydroxy propionic acid	25	3.873±0.006	3.919±0.01	3.86**	22.363
	30	3.896±0.009	3.942±0.008		22.681
	35	3.905±0.006	3.942±0.008		23.309
	40	3.942±0.008	3.992±0.006		23.932
	45	3.994±0.01	4.041±0.007		24.610
	50	4.028±0.009	4.076±0.006		25.217

*Reference [1] **Reference [17].

$$K_a^C = \frac{C\alpha^2}{1-\alpha} \tag{16}$$

In conductometry α is defined as

$$\alpha = \frac{\wedge_c}{\wedge_0} \tag{17}$$

Where Λ_c is equivalent conductance at some concentration C and Λ_0 is equivalent conductance at zero concentration or at infinite dilution. Λ_c = 1000L/c in which Λ is specific conductance in $S\text{-}cm^{-1}$. For uni-univalent electrolytes like HCOOH, CH_3COOH where ionic strength I=C, we have [1, 2, 7].

$$\log K_a^T = \log K_a^c - 2A\,(\alpha C)^{0.5} \tag{18}$$

At 25°C in aqueous solutions for univalent ions

$$\wedge = \frac{1.823\times10^6}{(\varepsilon_r T)^{3/2}} \tag{19}$$

Here ε_r is relative permittivity and T is the temperature in K. Eq. (18) then reduces to:

$$\log K_a^T = \log K_a^c - 1.0230\,(\alpha C)^{0.5} \tag{20}$$

Where K_a^T is thermodynamic and K_a^C is concentration ionization constant. K_a^T does not depend on concentration while K_a^C is concentration dependent.

Results and Discussion

Results summarized in Table 1 show the effect of temperature on pKa values and ΔG values of propionic acid and 2-hydroxypropionic acid. In case of propionic acid conductometric method is used to see the effect of temperature. As temperature increases from 25 to 50 °C with 5°C interval, pKa values increase from 4.842 to 4.988 and totle increase is 0.146 unit. Minimum increase of (0.008) in pKa values is marked between 25 to 30 °C while maximum increase of (0.104) unit is between 45 to 50 °C.

2-hydroxypropionic acid is analysed by potentiometric method. Potentiometric data shows that as the temperature increases from 25 to 50 °C, pKa values also increase from 3.896 to 4.028 and totle increse is 0.155 units. Minimum increase in pKa values is observed between 30 to 35°C which is 0.009 unit while maximum increase of 0.052 unit is noticed when temperature increases from 40 to 45 °C.

Both investigated compounds shows same parabolic curve when temperature increases. The equation of parabolic curves are as under:

(i) Propionic acid

$$y = 0.0003x^2 – 0.0158x + 5.0909 \qquad R^2 = 0.9211$$

(ii) 2-Hydroxypropionic acid

$$y = 0.0002x^2 – 0.0071x + 3.9909 \qquad R^2 = 0.9852$$

where $y = pK_a^T$ and x is the temperature in °C.

Results presented for both compounds show good agreement with the reported results [1,17]. Actually when an electrolyte is dissolved in a solvent (aqueous or non-aqueous), dissociation of solute is not independent, few forces become operative i.e. nature of electrolyte (strong or weak), hydrogen bonding, dielectric constant of solvent which varies with temperature, polarity of solvent in which electrolyte is dissolved and ionic size. Change in pKa values of particular compound is a result of all these effect which bring structural change in compound which in turn effect on ionization of substance as a result pKa values changes.

The effect of temperature on Gibb's free energy (ΔG) of propionic and 2-hydroxypropionic acid also follow parabolic equations. The equations are as under:

(i) Propionic acid

$$y = 0.0002x^2 + 0.0923x + 25.275 \qquad R^2 = 1$$

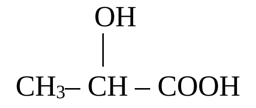
(ii) 2-Hydroxypropionic acid

$$y = 0.0012x^2 - 0.03x + 20.821 \qquad R^2 = 0.9969$$

Thermodynamic parameter (ΔG) values offer interesting insight into acid–base behaviour particularly with regards to solvation effect. ΔG values are calculated by using equation given in [18,19]. Both compounds show nearly same pattern but ΔG values are higher for propionic acid as compare to 2-hydroxypropionic acid.

A closer inspection of Table1 further shows that both pK_a^c and pK_a^T values are higher in case of propionic acid as compared to 2-hydroxypropionic acid. As hydroxyl group (-OH) is introduced in propionic acid, pKa values drops, although both compounds have same length of carbon chain.

$CH_3– CH_2 – COOH$
Propionic acid


$CH_3– \overset{\overset{OH}{|}}{C}H – COOH$
2-hydroxypropionic acid

pKa values drop in case of 2-hydroxypropionic acid is in accordance with the Hammett's equation [20,21].

$$\log K_i - \log K_o = \rho\sigma$$

where K_o is the acidity constant of unsubstituted acid and K_i is the acidity constant of substituted acid. The parameter σ is called the reaction constant, which is different for each substrate. According to Hammett's equation electron withdrawing (-OH) substituent decrease the pK_a values and have positive σ values while electron donating group ($-CH_3$) increase the pKa values and have negative σ values.

Keeping in view the Hammett's equation we can say that results presented in Table1 shows lower pK_a values when (-OH) group is substituted in 2-hydroxpropionic acid. The values of the substituent constants are dependent on the nature of substituents and position of substituent.

After going through the experimental data, it is concluded that as temperature increases pka values increases for both investigated compounds but pKa values of 2-hydroxypropionic acid (substituted compound) are lower as compare to propionic acid (unsubstituted compound) because a electron with drawing substitutent i.e. (-OH) is introduced in straight chain of propionic acid.

Experimental set up for conductometric data

Preparation of Propionic acid Solution

7.5 ml of propionic acid having purity of 99.5 percent and density 0.99 was taken in 100ml volumetric flask and volume was made upto mark with distilled water. It was standardized potentiometrically with 0.1 M sodium hydroxide. Again the series of molar solution of different concentration were prepared by successive dilution method.

Experimental Procedure

The instrument used was PHILIPS PW 9527 digital conductivity meter (4-digits) with an accuracy of ±0.15 percent. The cell used was PW 9550/60. Its cell constant was determined by standard 1M potassium chloride solution, and the cell constant was 0.872 cm^{-1}. Computer program was written in GW-BASIC language and alteration in this program continued till deviation in successive values of Λ_o was less then or equal to 10^{-9}.

Experimental set up for potentiometric data

Double distilled deionized conductivity water (1.0×10^{-6} Scm^{-1}) was used throughout the experiment. Stock solutions of 4×10^{-2} M 2-hydroxypropionic acid in water and 0.1 M sodium hydroxide were 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 PHILLIPS PW 9420 digital pH-Meter which was coupled with 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 ± 0.1°C.

Prior to experiment, pH meter was calibrated with 0.05 M potassium hydrogen phthalate (pH at 25 °C = 4.005) and potassium dihydrogen phosphate and disodium hydrogen phosphate, each 0.025 M ($pH_{25°C}$ = 6.863) in aqueous media [22].

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 [1]. For dispensing titrant, Mettler burette DV-10 accurate to ±0.01 ml was used.

The potentiometric measurments were performed on sample solution at different temperatures. The potentiometric data was analysed by computer program written in GW-BASIC for calculation of dissociation constants of monobasic acids.

Conclusion

It is concluded from the results that –OH group induction in propionic acid decreases the pK_a values. Both propionic acid and 2-hydroxypropionic acid show same parabolic curve when temperature increases.

Gibbs free energy (ΔG) values increases with increasing temperature and both compounds show nearly the same pattern but ΔG values are higher for propionic acid as compared to 2-hydroxypropionic acid.

References

1. A. Albert and E.P. Sergeant, "The determination of ionization constant", A Laboratory manual 3rd Edn., Chapman & Hall, London (1984).
2. A. Albert, "Selective Toxicity" 6th Edn., Chapman and Hall, London (1979).
3. G.B. Berlin and D.D. Perrin, "Technique of Organic Chemistry" (Ed. A. Weissbrger), Wiley Interscience, NewYork, 1981.
4. W.A. McBryde, Talanta, 21 (1974) 187.
5. R.W. Ramette, J. Chem. Edu., 44 (1974) 647.
6. G. Papanastasiou, I. Ziogas & I. Moumtsiz, Talanta, 35 (1986) 213.
7. A.G. Gonalez, D. Rosales, J.L.H. Ariza & A.G. Paraz, Talanta, 35 (1988) 249.
8. Saeeduddin, A.W.K. Khanzada & A.T. Mufti, Pak. J. Pharm. Sci. **9(1)** 21 (1996).

9. Saeeduddin, A.W.K. Khanzada & M.I. Bhanger, ACGS Chemical Research Communition (Austrlia). **6** (1997) 16.
10. Saeeduddin, A.W.K. Khanzada and M. Sharif, Jour. Chem. Soc. Pak., 24(3) (2003)153.
11. D.A. McInnes, T. Shedlovsky., J. Am. Chem. Soc., 54 (1932)1429.
12. Y. Gerasimor, V. Dreving, E. Eremin, A. Kiselev, V. Labeder, G. Panchenkor and A. Shlygin, " Physical Chemistry " Vol.2 Mir Publisher, Moscow (1974).
13. P. Debye and E. Huckel, Physikal Zeit., 24 (1823) 185.
14. P. Debye and E. Huckel, Physikal Zeit., 25 (1823) 145.
15. A.W. K.Khanzada, unpublished computer program.
16. E.P. Sergeant, "Potentiometry & Potentiometric Titration "John Wiley Press, New York (1984).
17. C. Robert and Weast, 67th Edition, CRC Hand Book of Chemistry and Physics CRC Press Inc, Florida, (1987), pp D-163.
18. E.J. King, "Acid- Base Equilibrium" Pergamon Press Oxford (1965) pp 225.
19. M. Jelikic, D. Veselionovic & P. Djurdevic., Talanta, 39 (1992) 665.
20. L.D. Hammett, J. Am. Chem. Soc., 59 (1937) 96.
21. Song. Li, M. Paleologou & W.C. Prude., J. Chromatogr., 29 (1991) 66.
22. H. Galster, "pH Measurment", VCH Weinheium Germany (1991) pp 53.