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An investigation of the impact of electrolytes on thermodynamic dissociation constant of pyruvic acid in aqueous media

Abdu MS[1], Aska AS[2], Faruq UZ[3], Dabai MU[4]
[1] Department of Chemistry, Federal University Gashua Yobe State, Nigeria
[2] Department of Chemistry, Aminu Saleh College of Education, Azare- Bauchi State, Nigeria
[3, 4] Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto, Nigeria

Abstract
The conditional dissociation constant (K_c) and thermodynamics dissociation constant (K_d) are use in solution chemistry to measure the extent of dissociation of molecules in solution. The thermodynamics dissociation constants of pyruvic acid were investigated using the principle of conductivity measurements in water (0:0), Sodium Chloride (1:1), Sodium Sulphate (1:2) and Lanthanum Chloride (3:1) supporting electrolytes in water as solvent. The degree of dissociation of pyruvic acid was determined through the measurements of molar conductance at specific dilution and molar conductance at infinite dilution. The degree of dissociation being a parameter through which the conditional and thermodynamic dissociation constants were determined was found to decrease with increase in concentration. The thermodynamics dissociation constant (K_d) was observed to increase with increase in charge ratio of the supporting electrolytes except, for lanthanum chloride which may possibly due to non participation of the hydrated lanthanum ions. The result revealed that in water(0:0) electrolyte, the K_d is 1.48 x 10^{-4} /moldm^{-3}, in 1:1 electrolyte the K_d is 1.51 x 10^{-4}/moldm^{-3}, in 1:2 electrolyte the K_d is 1.62 x 10^{-4}/moldm^{-3} while in 3:1 electrolyte the K_d is 0.79 x10^{-4}/moldm^{-3}. The change in ionic strength of the electrolytes was found to influence the values of thermodynamic dissociation constants of pyruvic acid in various supporting electrolyte as obtained.

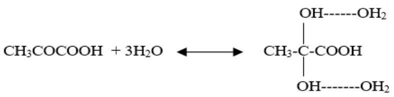
Keywords: investigation, pyruvic acid, electrolyte, thermodynamics, dissociation constant, conductivity measurement

Introduction

2-oxopropanoic acid commonly known as pyruvic acid occurs as an intermediate product in the metabolism of carbohydrates and proteins. Also, pyruvic acid is easily broken down to acetaldehyde and carbon dioxide by an emzyme decarboxylase, and through gluconeogenesis, pyruvic acid is used in the synthesis of glucose (Jaimes, 2015) [3]. Another anaerobic alternative for pyruvic acid is that it can be converted into acetaldehyde and then into ethanol. This kind of reaction generally occurs in yeast. In the first reaction, pyruvic acid releases carbon dioxide as it becomes acetaldehyde. That process, in yeast, generates the carbon dioxide that is necessary for causing breads and baked goods to rise before they are baked. In the second reaction, an aldehyde is converted into an alcohol. This is another reduction reaction (Jaimes, 2015) [3].

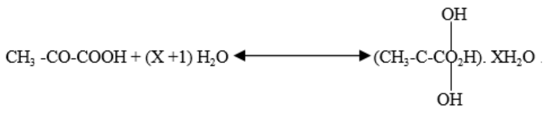
$$CH_3COCOOH \longrightarrow CH_3CHO + CO_2 \longrightarrow CH_3CH_2OH \qquad 1.0$$

Pyruvic acid is highly soluble in water. According to Ogota and Kawasaki (1970), the keto group is hydrolyze and takes in three (3) molecules of water as shown in the following equation:

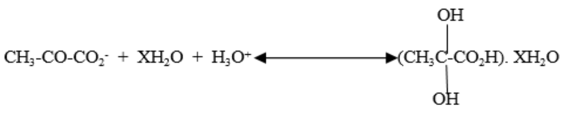


$$CH_3COCOOH + 3H_2O \longleftrightarrow CH_3\text{-}\overset{OH\text{------}OH_2}{\underset{OH\text{-------}OH_2}{C}}\text{-}COOH \qquad (1.1)$$

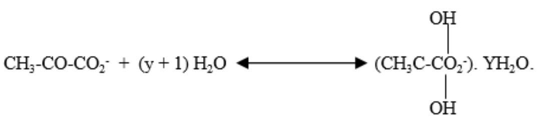
Khan, *et al.* (1995) [5] also have shown by NMR that at P_{H} =1, less than 20% of the total concentration of pyruvic acid exist in enol form. Gold and Griffiths (1967) [2] have determined the relative concentration of pyruvic acid and its hydrate at P_H=1 by rexation method. Khan, *et al.* (1995) [5] also reported the mechanism of pyruvic acid hydrolysis and evaluated the Pka values of both hydrated and pure pyruvic acid. Following the acid properties of the pyruvic acid and $_P$H of the reaction media, they were able to established three possible equilibria for its hydrolysis according to the following equations:



$$CH_3\text{ -CO-COOH} + (X+1)\,H_2O \longleftrightarrow (CH_3\text{-C-}\overset{OH}{\underset{OH}{C}}O_2H).\,XH_2O \qquad (1.2)$$



$$CH_3\text{-CO-}CO_2^- + XH_2O + H_3O^+ \longleftrightarrow (CH_3\overset{OH}{\underset{OH}{C}}\text{-}CO_2H).\,XH_2O \qquad (1.3)$$



$$CH_3\text{-CO-}CO_2^- + (y+1)\,H_2O \longleftrightarrow (CH_3\overset{OH}{\underset{OH}{C}}\text{-}CO_2^-).\,YH_2O. \qquad (1.4)$$

At $_P$H< 3, the system is limited to an equilibrium (equation1.2), while at high $_P$H values equilibria (eq. 1.3 and

1.4) are possible. The reasons adduced by Khan *et al.*, (1995) [5]; suggests an increased in the quantity of pyruvic acid and its conjugate base, and possibly the decrease in the hydration due to weak influence of electron withdrawing of the unprotonated carboxylate group. However, Khan *et al.* 1995 [5]; were able to established the fact that equilibrium (1.4) becomes predominant with the formation of the 2,2. dihydroxy propionate ions as the $_P$H of the media continues to increase from 2.18 to 3.60. Fundamentally, ionogen RH such as pyruvic acid in solvents (water) gives rise to the following equilibria:

$$RH\,(aq) \longrightarrow k_1\ R^-H^+(aq) \quad k_c \longleftrightarrow R^-(aq) + H_3O^+(aq) \tag{1.5}$$

Where the ionization and dissociation constants, K_i and K_c respectively are defined by

$$K_i = \frac{[R^-H^+(aq)]}{[RH(aq)]} \tag{1.6}$$

Where α is the degree of dissociation. The thermodynamic dissociation constant K_D by definition is

$$K_c = \frac{[R^-(aq)]\,[H_3O^+(aq)]}{[R^-H^+(aq)]} = \frac{\alpha^2 C}{1-\alpha} \tag{1.7}$$

$$K_d = \frac{K_c \gamma^+ \gamma^-}{\gamma_{RH}} \tag{1.8}$$

Where $\gamma+$ $\gamma-$ and γ_{RH} are the activity coefficients of cation, anion and the pyruvic acid molecule respectively, while the activity coefficient of pyruvic acid (γ_{RH}) is assumed to be unity. Thus, equation 1.8 approximates to:

$$K_d = K_c \gamma^2_{\pm} \tag{1.9}$$

Where $\gamma^2_{\pm}$ is the mean activity coefficient of the ions in solution. Also following the Debye Huckel consideration of ionic species at infinite dilution, the following equation is well known (Shoemaker, *et al.* 2009) [12].

$$\text{Log } \gamma\pm = -A\,[Z+\ Z-]\, I^{1/2} \tag{1.10}$$

However at higher concentration of ionic species in which the electrostatic forces are significant the equation (1.11) assumes its proper value:

$$\text{Log } \gamma\pm = \frac{-A[Z+\ Z-]\, I^{1/2}}{1+ B\, a^{\circ}\, I^{1/2}} \tag{1.11}$$

Where the A and B are experimental constants and "a°" is the Debye length of the ionosphere in the solution. Following the rearrangement through logarithmic equation (1.9) and substituting equations1.10 and 1.11 separately gives the following relations:

$$\text{Log } K_c = \text{Log} K_d + A[Z+,\ Z-] I^{1/2} \tag{1.12}$$

$$\text{And Log } K_c = \text{Log } K_D + \frac{A[Z+\ Z-]\, I^{1/2}}{1\ +\ B\, a^{\circ}\, I^{1/2}} \tag{1.13}$$

Where all the parameters retain their usual meanings as defined above. In our attempt to evaluate equations 1.12 and 1.13, used is made of well-known relations (Shoemaker, *et al.* 2009) [12].

$$\Lambda = \frac{10^3\, k}{C} \tag{1.14}$$

Where Λ and k are the molar conductivity and specific conductivity respectively of the ionic species of known concentration, C. Thus, various values of Λ are plotted against the concentrations according to Kohlrausch's law (Moore, 1963) [7]:

$$\Lambda = \Lambda_o - z\, C^{1/2} \tag{1.15}$$

Where, Λo is the molar conductivity at infinite dilution of the ions and z, being the experimental constant. Following the values of Λo, the degree of dissociation, α is evaluated for each concentration via the relation:

$$\alpha = \Lambda/\Lambda o \tag{1.16}$$

From which the conditional dissociation constant k_c and the ionic strength $I = 1/2\sum Ci\ Zi^2$ are used to evaluate K_d in equation (1.12). Onuchukwu and Waziri, (1987) [10] have reported the thermodynamic dissociation constant of o-substituted benzoic acid in aqueous medium from this principle. Although, most of the organic molecules are sparingly soluble in water and volatile for any rise in temperature, pyruvic acid is very much soluble in water. This is possible due to affinity that exists between the acid and the water molecules. On dissociation, it produces limited quantity of hydronium ions (H_3O^+) in solution as expected from the properties of an ionogen given by the dissociation equation:

$$\underset{\text{Pyruvic acid}}{CH_3\text{-}CO\text{-}COOH} \xleftrightarrow{+H_2O} \underset{\text{pyruvate ion}}{CH_3\text{-}CO\text{-}COO^-} | + \underset{\text{Hydronium ion}}{H_3O^+} \tag{1.17}$$

Pocker and Meany (1969) [11] have evaluated the thermodynamic parameters for the dissociation of pyruvic acid in aqueous medium at $_P$H< 1.0. The determination of the Pk_a of perhydroxyl ions through conductance and $_P$H measurements using conductivity meter and the determination of molar equivalent conductance for various concentrations of the acid has also been reported (Jetse *et al.*, 2013) [4].

Material and methods

Reagents

Pyruvic acid, Sodium chloride, Sodium sulphate, Lanthanium chloride, Potassium chloride, Sodium hydroxide, Hydrogen peroxide, Chloroplatinic acid, Buffer tablets, distilled water, deuterium oxide solution and acidified water.

Materials

Platinium electrodes, conductance cells, PH meter, pipette, volumetric flasks, distillation apparatus, thermometer and vacuum pump.

Methodology

Purification of pyruvic acid

Purification was done by distillation method. Fractional distillation under reduced pressure was carried out after setting upof distillation apparatus. The heating was commenced at 28°C and the Edwards High Vacuum pump Model ED 50 was set between 2.5-4mm Hg pressure and acid was collected at 42°C in order to determine the boiling point of pyruvic acid the heating continued after 15minutes, vapours were observed at 165°C which indicated good purity of the pyruvic acid.

Preparation of standard solution of pyruvic acid

Standard solution of pyruvic acid was prepared by pipetting out 0.5ml of the acid in to a one-litre volumetric flask and the solution with distil water up to a litre mark. The solution was shaken adequately to ensure that the acid has dissolved completely and the concentration of 6.7 X 10^{-3} M was obtained. Further dilutions of these solutions were carried out by taken, 1,2,3,4 up to 9ml each separately into 9 different 100ml volumetric flasks and the made the solution with distil water up to the mark to obtain 67-600 *micromolar* concentration of the acid. According GN Lewis the experimentally determined value of concentration whether molecules or ions in solution is less than the actual concentration (Shoemaker, *et al*., (2009) [12]. This is because the effective number of cations and anions in solution becomes less as they tend to form ion pair due to strong electrostatic attraction. Thus the effective concentrations of ions become less than the actual concentration. In view of this, therefore, the actual concentration(C) has to be replaced with the effective concentration for accurate experimental work. If the effective concentration which is also termed activity is denoted by "a", activity coefficient ɣ may be defined as the ratio between the effective concentration "a" and the actual concentration C of the molecules or ions in solution i.e.

$$\gamma = \frac{\text{effective Concentration}}{\text{Actual concentration}} = \frac{a}{c}$$

$$\gamma = \frac{A}{C}$$

Therefore, $a = \gamma C$

From the literature, the activity coefficient of pyruvic acid was found to be 0.996 which was utilized in all the calculations where necessary.

Preparation of standard solution of supporting electrolytes

Standard solutions of the supporting electrolytes were prepared from BDH grade reagents as follows: 0.0584, 0.142, and 0.3714g of Sodium chloride, Sodium sulphate and Lanthanum chloride respectively were dissolved separately in 100ml distilled water to obtain the required 10^{-2}M concentration of each of these salts. Also further dilutions of these supporting electrolytes were carried out by taken 20ml of each of the above 10^{-2}M solutions into various volumetric flasks and making up the solution to a litre mark to obtain another set of supporting electrolytes of 20 micro-molar concentration of each salt. Also, solutions of sodium hydroxide and hydrogen peroxide from BDH grade reagents were prepared as follows: 20g and 60ml of sodium hydroxide and hydrogen peroxide respectively were dissolved separately in 1000ml volumetric flask and the made the solutions up to a litre mark with distilled water to obtain 0.5M and 5M concentrations of sodium hydroxide and hydrogen peroxide respectively.

Pyruvic acid in supporting electrolytes solutions

Other dilutions of 6.7 X 10^{-3}M concentration of pyruvic acid prepared above in various supporting electrolytes prepared were carried out as follows: 1, 2, and 3 up to 9ml series of 10-3 M Concentration of pyruvic acid were measured into nine different 100ml volumetric flasks. Sodium chloride of 200micro molar concentration prepared was used as solvent to obtain 67-600micromolar concentrations of acid in sodium chloride solution. The same process was repeated using different electrolyte solutions of 200micromolar concentrations as the solvents i.e. sodium sulphate and Lanthanum chloride solutions respectively.

Conductance measurement

The conductance of distilled water and pyruvic acid in supporting electrolyte solutions prepared in 3.5.2 were measured as follows: the cell of the calibrated digital conductivity meter model (PT 1-58) was dipped into 50ml of distilled water and a conductance of 13.6 X 10^{-6} scm^2mol^{-1} was obtained. By rinsing the cell with distilled water after every measurement, the conductance of each of the nine different concentrations of pyruvic acid in sodium chloride solution was measured to obtain the required $10^{-6}scm^2mol^{-1}$ conductance. The same procedure was repeated using the remaining supporting electrolyte solutions.

Results and discussion

Table 1: Variation of Molar conductivity at specific dilution and the square root of molar concentration of pyruvic acid in water (0:0)

CONC.($moldm^{-3}$) PYRUVIC ACID	$CONC^{1/2}$ ($C^{1/2}$ /$mol^{1/2}dm^{-3/2}$) X 10^{-2}	Λ(Scm^2mol^{-1})
0.56	0.75	8.60
1.00	1.00	7.45
1.96	1.40	6.35
2.25	1.50	5.40
3.06	1.75	4.30
5.76	2.40	3.00

Table 2: Variation of Molar conductivity at specific dilution and the square root of molar concentration of pyruvic acid in Sodium chloride electrolyte (1:1)

CONC.(moldm^{-3}) Pyruvic ACID	**CONC$^{1/2}$ (C$^{1/2}$ /mol$^{1/2}$dm$^{-3/2}$) X 10^{-2}**	**Λ(Scm^{2}mol^{-1})**
0.64	0.80	11.10
1.00	1.00	10.30
1.28	1.13	9.80
2.40	1.55	9.30
3.80	1.95	8.50
4.00	2.00	7.90

Table 3: Variation of Molar conductivity at specific dilution and the square root of molar concentration of pyruvic acid in sodium sulphate electrolyte (1:2)

CONC.(moldm^{-3}) Pyruvic Acid	**CONC$^{1/2}$ (C$^{1/2}$ /mol$^{1/2}$dm$^{-3/2}$) X 10^{-2}**	**Λ(Scm^{2}mol^{-1})**
0.49	0.70	13.90
0.81	0.90	13.00
1.96	1.40	12.10
2.25	1.50	11.30
3.06	1.75	10.50
3.80	1.95	9.80

Table 4: Variation of Molar conductivity at specific dilution and the square root of molar concentration of pyruvic acid in lanthanum chloride electrolyte (3:1)

CONC.(moldm^{-3}) Pyruvic Acid	**CONC$^{1/2}$ (C$^{1/2}$ /mol$^{1/2}$dm$^{-3/2}$) X 10^{-2}**	**Λ(Scm^{2}mol^{-1})**
0.30	0.55	14.00
1.96	1.40	12.40
2.25	1.50	11.20
2.72	1.65	10.40
3.06	1.75	9.50
4.00	2.00	8.60

Table 5: Variation of Log Kc and square root of ionic strength of pyruvic acid in water (0:0)

K_c X 10^{-4}	LogK_c	I	I$^{1/2}$ x 10^{-3}
1.396	-3.8550	0.0914	8.36
1.326	-3.8775	0.0326	10.64
1.175	-3.9300	0.0418	17.48
1.078	-3.9675	0.0485	23.56

Table 6: Variation of Log Kc and square root of ionic strength of pyruvic acid in Sodium chloride (1:1)

K_c X 10^{-4}	**LogK_c**	**I**	**I$^{1/2}$ x 10^{-3}**
7.0794	-3.150	0.0994	9.88
6.0604	-3.217	0.0349	12.16
5.1880	-3.285	0.0380	14.44
4.2904	-3.3675	0.0399	15.96
3.3690	-3.4725	0.0427	18.24

Table 7: Variation of Log Kc and square root of ionic strength of pyruvic acid in Sodium sulphate (1:2)

K_c X 10^{-4}	LogK_c	I	I$^{1/2}$ x 10^{-3}
4.5973	-3.3375	0.0338	11.40
4.1448	-3.3825	0.0444	19.76
3.6728	-3.435	0.0493	24.32
3.2546	-3.4875	0.0523	27.36
2.7384	-3.5625	0.0551	30.40

Table 8: Variation of Log K_c and square root of ionic strength of pyruvic acid in Lanthanum chloride (3:1)

K_c X 10^{-4}	**LogK_c**	**I**	**I$^{1/2}$**
5.3703	-3.270	0.0485	23.56
4.8417	-3.315	0.0544	29.64
4.1448	-3.3825	0.0641	41.04
3.6728	-3.435	0.0669	44.84
3.1441	-3.5025	0.0702	49.40
2.2259	-3.6525	0.0724	52.44

Table 9: The effect of electrolytes on thermodynamics dissociation constant (K_D)

Electrolytes	**TYPE**	**K_d x10^{-4} moldm^{-3}**
Water(H_2O)	0:0	1.48
Sodium chloride (NaCl)	1:1	1.51
Sodium sulphate (Na_2SO_4)	1:2	1.62
Lanthanum Chloride ($LaCl_3.7H_2O$)	3:1	0.79

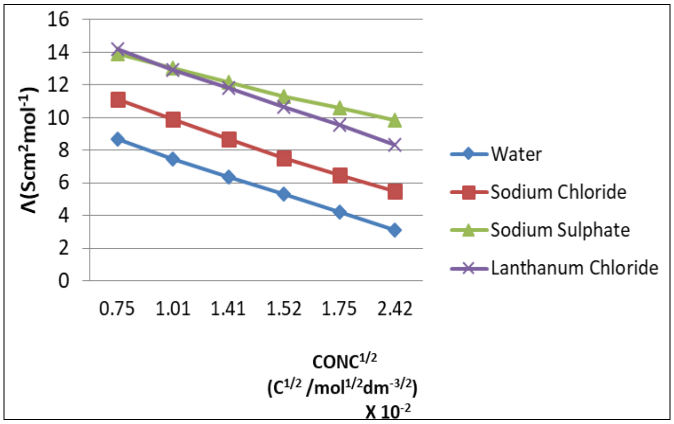


Fig 1: shows the variation of molar conductance, Λ /S cm^2 mol^{-1} vs c$^{1/2}$/mol$^{1/2}$ dm$^{-3/2}$ of pyrubic acid in 0:0, 1:1, 1:2 and 3:1 supporting electrolytes at 28^{0}C

NB: in fig.1 above, the curves were extrapolated to meet the y-axis in order to determine the values of Molar conductance at infinite dilution which were used in calculating the degree of dissociation.

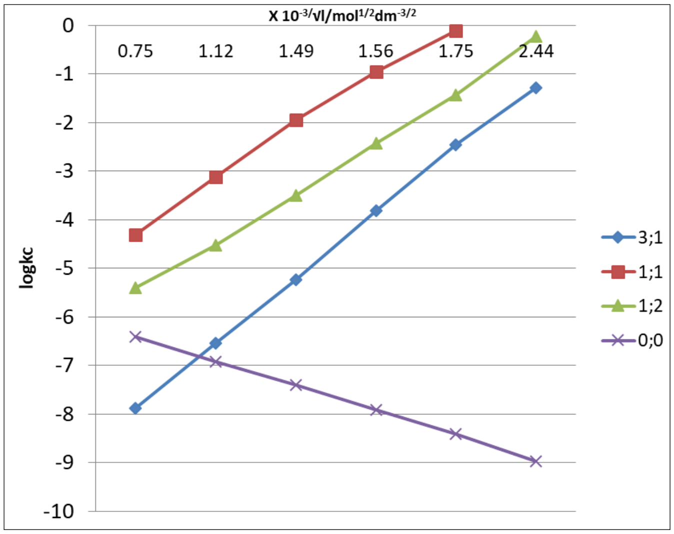


Fig 2: shows the variation of logk$_c$ vs I$^{1/2}$/mol$^{1/2}$dm$^{-3/2}$ of pyruvic acid in 0:0, 1:1, 1:2 and 3:1 supporting electrolytes at 28^{0}C

Discussion of results

The ability of an acid to undergo complete dissociation is known by its degree of ionization (α) which is obtained through molar conductance at specific and infinite dilutions, Λ and Λ_o respectively as contained in equation 1.16. Molar conductance at infinite dilution is evaluated through the plot of molar conductance at specific dilution against Square root of concentration, ($C^{1/2}$) as shown in fig. 1. In this work, a decrease in molar conductance (Λ) with increase in concentration of pyruvic acid in both water and the supporting electrolytes studied is shown in fig 1. Consequently, degree of dissociation being a parameter through which the conditional and the thermodynamic dissociation constants are determined is found to decrease with increase in concentration (Onuchukwu and Waziri, 1987) [10]. This is possibly due to the fact that the electrostatic attraction between the ions is so great that ion pairing occurred which overcome the tendency for the ions to move around as separate particles each with its own translational degrees of freedom. Since degree of dissociation (α) is a function of conductivity which also depends on ionic mobility in solution, ion pairing will reduce the mobility and consequently the degree of dissociation (Marcus and Hefter, 2006). Furthermore, salvation may likely cause the formation of hydrogen bond between the molecules or ions and the water molecules. This will also affect the mobility of ions or molecules in solution resulting in the low value of degree of dissociation (Afanas'ev, 2011). Ionic strength being both concentration dependant and ionic charge by its definition is found in this work to increase with increase in the charge ratio of the supporting electrolytes. Thus, increase in population of ionic species in solution is mainly due to dissociation behavior of the supporting electrolytes and therefore explained increased in ionic strength (Khan, *et al*., 1995) [5]. This change in ionic strength by the charge ratio of supporting electrolytes is observed to influence the values evaluated for thermodynamic dissociation constants of pyruvic acid in various supporting electrolytes a shown in fig 2.

Conditional and thermodynamic dissociation constants K_c and K_d respectively are used in solution chemistry as a measure of the extend of dissociation of molecule in solution. Used is made of these two terms also to defined equilibrium constant, when a solute attains equilibrium in contact with a solvent such as water. While salvation and ionosphere have effects on the thermodynamics dissociation constant K_d, conditional dissociation constant K_c is solely concentration dependant. The conditional dissociation constant K_c is observed to increase with increase in concentration and this is due to the fact that in weak electrolyte there is a decrease in molar conductance(Λ) with the increase in concentration(Khan, *et al*., 1995) [5]. Since ionosphere formation in ionic solution is concentration dependant, it is possible that the preference for conditional dissociation constant K_c for the thermodynamic dissociation constant K_d is mainly due to ionic interaction in solution because K_c has a value for each concentration while K_d is obtained at infinite dilution for series of ionic concentrations. This trend was observed in Figure 2 when various values of K_d where evaluated using equation (1.12). Thermodynamic dissociation constant K_d shows increase with increase in charge ratio from the solvent (water) to Sodium sulphate except for lanthanum chloride which is possibly due to its hydrolysis in aqueous media. The formation of hydrated lanthanum ions possibly minimized the formation of ionosphere on the pyruvic acid ions. This phenomenon may be responsible for its low value of K_d as compared with other supporting electrolytes as shown in table 9. This behavior can be explained by the fact that the thermodynamic dissociation constant K_D values are not influence by the ionosphere at infinite dilution but are affected more by Solvation (Afanas'ev, 2011). These phenomena would enhance complete dissociation and may explain the observed increase in K_d. Although conditional dissociation constant K_c increases with increase in concentration, higher values are observed for K_d in this study. These may be due to the fact that K_c has a value for each concentration while K_d is obtained at infinite dilution. This trend is observed in fig. 2 in which variation of K_c with ionic strength was investigated during the evaluation of K_d.

Thermodynamic dissociation constant K_d is shown to be influenced by activity coefficient (ɣ) which takes into account the electrostatic interaction of ions in solutions which discriminate ideal solution from real solution. This is typifies by equation 1.12 which makes distinction between K_d and K_c The value of K_d obtained from equation 1.12 in this work for pyruvic acid dissolved in water is 1.48 x10^{-4}. The value was found to be higher than K_c values obtained from equation 1.7 for series of concentrations of pyruvic acid in water.

When supporting electrolytes were introduced into solution of pyruvic acid, K_c values were observed to be higher than K_d values. It is possible to argue for this increase, because K_c being concentration dependant, increases with increase in charge ratio and consequently formed a strong ionosphere around the central ion (pyruvic acid). The ionosphere formation arises from effective dissociation and possibly explains the observed increase in K_c with introduction of the supporting electrolyte which provides a preponderous ions in solution (Jetse *et al*, 2013) [4].

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