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Research article

Dissociation Constant Studies of 2-Substituted 4-Formylbenzoic Acid based on Conductometric Parameters using Fuoss-Hsia Theories

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Abstract

The dissociation constant is a quantitative measure of the strength of an acid in solution. This study examines dissociation constant for the series substituted acids like Ortho-alkoxy-4-formylbenzoic acid. The use of (2-methoxy ethanol) as a solvent contributed to the study expected to form free ions or solvent separated ion pair which has been studied with the use conductometric method at different temperatures ranged from 293.15 to 318.15K. The study aims at figuring out dissociation constant, equivalent conductance at infinity dilution, and Walden product by minimization technique using Fuoss-Hsia for both (Modified and Complete) equations. It has been found in the results that the calculated values based on statistical sum square (different between practical and theoretical values) is equivalent conductance at infinity dilution and dissociation constant. It has also been observed that increase the temperature leads to the increase of the molar conductance at infinity dilution, and the increase in association. Moreover, the substituted alkoxy group also affected dissociation of compounds. In this study, the thermodynamic parameters (ΔH^o, ΔG^o and ΔS^o) have also been evaluated and discussed. Finally, the effect of substituent groups on rate of dissociation was studied and explained with agreement to the principles of mesomeric(M) and Inductive effect(I) of substituent groups on dissociation constant.

Keywords: *Conductometric; dissociation constant; fuoss-Hsia theories; minimization technique; thermodynamic parameters.*

1. Introduction

Many studies on thermodynamics and dissociation constant have been conducted in connection with conductometry with the use of many equations [1-6]. Friedrich Kohlrausch (1840–1910), a German chemist, initially proposed the Kohlrausch equation as the outcome of extensive experimental effort.

$$\Lambda = \Lambda_0 - K\sqrt{C} \qquad (1)$$

where Λ is the molar conductance, Λ_0 is molar conductance in the limit of zero concentration when the ions do not interact with each other, K is a coefficient related to the stoichiometry of the electrolyte, and C is the concentration of the electrolyte [7]. The inductive effect of the substituent is transmitted to the carboxyl group in two rather different ways. Most frequently, the substituent is regarded as causing shifts in the average distributions of the bonding electrons along the chain of atoms in the carboxyl proton. This produces a succession of electron shifts along the chain of atoms which leads to electron-attracting substituent that increases the acid strength by making it more energetically feasible for the –OH [8]. The equations:

$$\Lambda=\Lambda_0-S\sqrt{C} + E^{'} c\ln c + Jc-K_A\Lambda_{0c} \qquad (2)$$

Can be used to calculate dissociation constant

$$(K_d=1/K_A) \quad . \qquad (3)$$

where Λ, Λ_0 are equivalent conductance, equivalent conductance at infinity dilutions respectively, $E^{'}$ is constant factor, Jc is a term from long-range interaction and $K_A\Lambda_{0c}$ term from pair formation near in concentration (c)[9].
According to Arrhenius's original definition, an acid is a substance that dissociates in aqueous solution, releasing the hydrogen ion H^+ (a proton):

$$[HA \rightleftharpoons A^- + H^+] \qquad (4)$$

The equilibrium constant for this dissociation reaction is known as dissociation constant [10-12]. The stability of substitution in 4- position of benzoic acid, and stability of the mentioned compound at different solvent was estimated [13, 14]. The conductometric study of benzoic acid has been studied with the use of many equations for finding dissociation constant, thermodynamic parameters and equivalent conductance at infinity dilution [15, 16]. The other studies show that the temperature, type of electrolytes, solvents and conductometric equations play an important role in shaping conductometric curve at different solvents [17, 18]. The study of dissociation constant with thermodynamic parameters in a mixture solvent illustrates that the increase of pK values causes solvation stabilization of a proton greater than others [19]. The molar conductance

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at infinity dilution(Λ_o), dissociation constants (Kd) were determined with using theoretical conductance equations of the complete and modified forms of Fuoss-Hsia [20-22].

2. Materials and Methods

The measurements are made at a range of temperature between 283.15-318.15K with the instrument named OKATON conductometer type CON 510 BENCHTOP METER audio frequency, and all the stock solutions are prepared by weight and measurements with the manipulation of the weight dilution technique. The Table 1 shows the experimental conductance for compounds 1, 2, 3 and 4 (Aladdin). The instrument accuracy for conductivity measurements is about ±0.05%. The cell constant (as determined by standard solutions of purified potassium chloride (Sigma-Aldrich)) is 0.9993. The method used for measuring cell constant and conductance has been described in [23]. The compounds 1, 2, 3 and 4 in (Figure 1) that is used in this study is prepared by Sigma-Aldrich Company. This study aims at finding dissociation constant of weak electrolytes 1, 2 and 3 compared with compound number 4. Then it extends to estimate thermodynamics parameters to prove the interaction between the ion and solvent to produce ion pair or solvent separate ion pair consequently conductometric study results in finding Walden product depending on the increase of temperature and viscosity, and this attributes to the dielectric friction constant for the compounds with viscosity, the high viscosity showed the low value of conductivity.

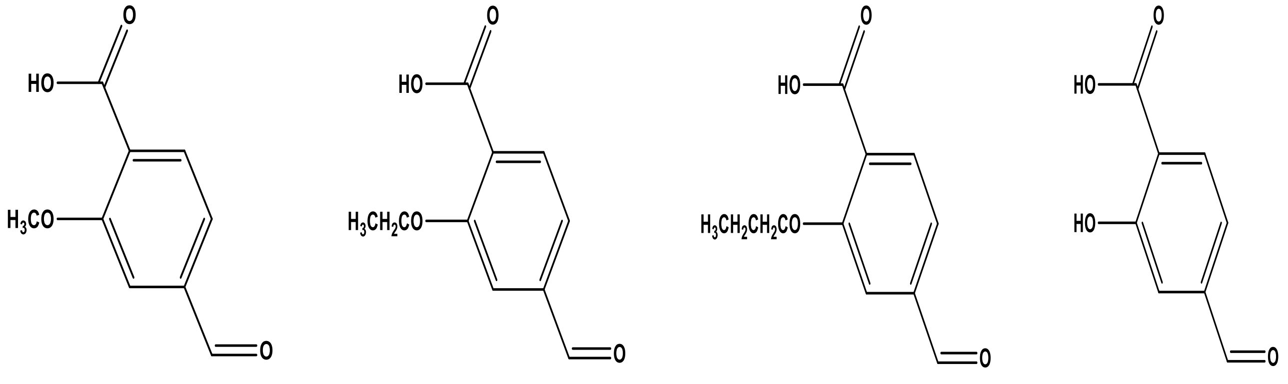
2.1 Computational Study

Example of minimization program (Figure 2). In the present work, all program was written in Fortran power station 4, worked under windows 10, used to minimize the measure conductance data which is fed in as N pair of C_i/Λ_i values, the best fitted values of the two parameters K_A ($K_A=1/K_d$) and Λ_o which are usually obtained as follows: K_A runs from an initial value of KA to KMAX in steps of DKA and Λ_o runs from an initial value of L0 to L0MAX in steps of DL0, with respect to complete Fuoss-Hsia (Fuoss and Hsia, 1967) given as an example here, and the input is needed in the following order: ETA (Viscosity of solvent), D (Dielectrical constant of solvent), T (absolute temperature) Z (valency of electrolyte), L0 (Initial $\Lambda_{o\ \text{value}}$), K_A (Initial K_A value), N (C_i/Λ_i pair numbers) and C(I, J) (N pairs of C and Λ data). The output consists of the sum square S^2 , between calculated and measured conductances and the corresponding values of KA, Λ_o.

3. Results and Discussion

This work aims at examining the dissociation Constant of Some Ortho Substituted 4-Formylbenzoic Acid (where substituted are: $-OCH_3$, OCH_2CH_3, $-OCH_2CH_2CH_3$, -OH) Compounds based on Conductometric Parameters which is calculated with the use of Fuoss-Hsia Theories of both modified and complete at different temperatures. Molar conductance was measured, and it has been foundthat corresponding concentration in mol.dm^{-3} that the temperature ranges between 283.15-318.15K, as it is given in Table 1. The interpretation of the characteristic parameters of a weak electrolyte solution from conductance data using minimization technique is adopted to find dissociation constant (Kd), Molar conductance at infinity dilution (Λ_o).

For the data analysis, this study draws on C_i (Concentration), Λi (equivalent conductance) (i=1, 2,..,N) with the use of a Fortran power station-4X- computer program. The output results of minimization technique for the best fit values of the three parameters: K_d, Λ_o depending on sum square (S^2), standard deviation (σ) and Walden product as they are listed in Tables (2, 3, 4 and 5). In Figures (3, 4, 5 and 6), are curves of molar conductance versus square root of concentration at different temperature ranges between 283.15-318.15 K for these electrolytes. The measured Λ_0, K_d was obtained from Minimization technique, the temperature effect on the solvent solute interaction is shown in Table 1, as the temperature increased the molar conductance increased of at interval.



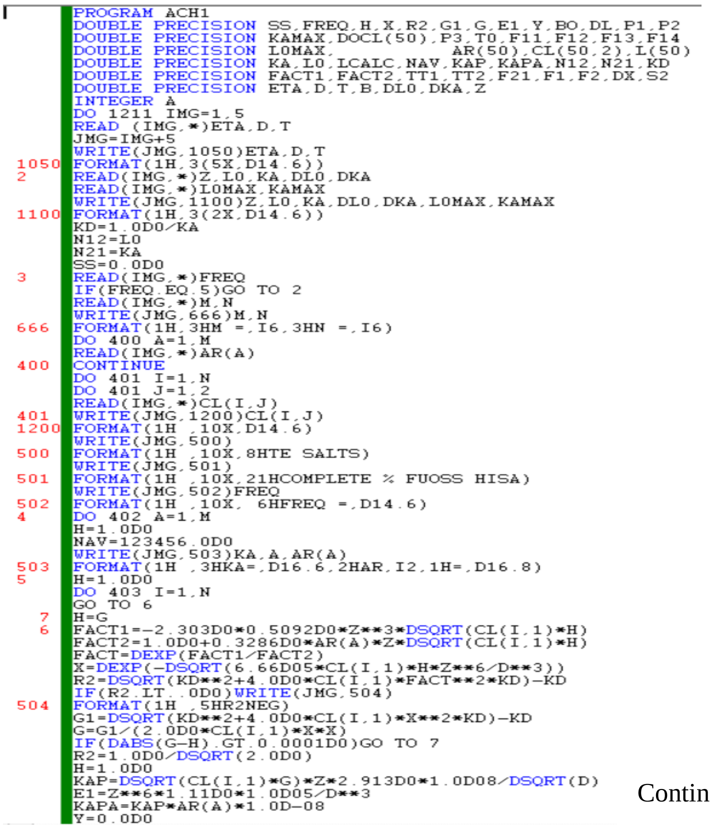
4-formyl-2-methoxybenzoic acid
1

2-ethoxy-4-formylbenzoic acid
2

4-formyl-2-propoxybenzoic acid
3

4-formyl-2-hydroxybenzoic acid
4

Figure 1. Structure of compounds under study.



```
      PROGRAM ACH1
      DOUBLE PRECISION SS,FREQ,H,X,R2,G1,G,E1,Y,BO,DL,P1,P2
      DOUBLE PRECISION KAMAX,DOCL(50),P3,T0,F11,F12,F13,F14
      DOUBLE PRECISION L0MAX,          AR(50),CL(50,2),L(50)
      DOUBLE PRECISION KA,L0,LCALC,NAV,KAP,KAPA,N12,N21,KD
      DOUBLE PRECISION FACT1,FACT2,TT1,TT2,F21,F1,F2,DX,S2
      DOUBLE PRECISION ETA,D,T,B,DL0,DKA,Z
      INTEGER A
      DO 1211 IMG=1,5
      READ (IMG,*)ETA,D,T
      JMG=IMG+5
      WRITE(JMG,1050)ETA,D,T
1050  FORMAT(1H,3(5X,D14.6))
2     READ(IMG,*)Z,L0,KA,DL0,DKA
      READ(IMG,*)L0MAX,KAMAX
      WRITE(JMG,1100)Z,L0,KA,DL0,DKA,L0MAX,KAMAX
1100  FORMAT(1H,3(2X,D14.6))
      KD=1.0D0/KA
      N12=L0
      N21=KA
      SS=0.0D0
3     READ(IMG,*)FREQ
      IF(FREQ.EQ.5)GO TO 2
      READ(IMG,*)M,N
      WRITE(JMG,666)M,N
666   FORMAT(1H,3HM =,I6,3HN =,I6)
      DO 400 A=1,M
      READ(IMG,*)AR(A)
400   CONTINUE
      DO 401 I=1,N
      DO 401 J=1,2
      READ(IMG,*)CL(I,J)
401   WRITE(JMG,1200)CL(I,J)
1200  FORMAT(1H ,10X,D14.6)
      WRITE(JMG,500)
500   FORMAT(1H ,10X,8HTE SALTS)
      WRITE(JMG,501)
501   FORMAT(1H ,10X,21HCOMPLETE % FUOSS HISA)
      WRITE(JMG,502)FREQ
502   FORMAT(1H ,10X, 6HFREQ =,D14.6)
4     DO 402 A=1,M
      H=1.0D0
      NAV=123456.0D0
      WRITE(JMG,503)KA,A,AR(A)
503   FORMAT(1H ,3HKA=,D16.6,2HAR,I2,1H=,D16.8)
5     H=1.0D0
      DO 403 I=1,N
      GO TO 6
   7  H=G
   6  FACT1=-2.303D0*0.5092D0*Z**3*DSQRT(CL(I,1)*H)
      FACT2=1.0D0+0.3286D0*AR(A)*Z*DSQRT(CL(I,1)*H)
      FACT=DEXP(FACT1/FACT2)
      X=DEXP(-DSQRT(6.66D05*CL(I,1)*H*Z**6/D**3))
      R2=DSQRT(KD**2+4.0D0*CL(I,1)*FACT**2*KD)-KD
      IF(R2.LT..0D0)WRITE(JMG,504)
504   FORMAT(1H ,5HR2NEG)
      G1=DSQRT(KD**2+4.0D0*CL(I,1)*X**2*KD)-KD
      G=G1/(2.0D0*CL(I,1)*X*X)
      IF(DABS(G-H).GT.0.0001D0)GO TO 7
      R2=1.0D0/DSQRT(2.0D0)
      H=1.0D0
      KAP=DSQRT(CL(I,1)*G)*Z*2.913D0*1.0D08/DSQRT(D)
      E1=Z**6*1.11D0*1.0D05/D**3
      KAPA=KAP*AR(A)*1.0D-08
      Y=0.0D0
```

Continued…

Figure 2. Fuoss Hsia program for finding Kd.

Table 1. Experimental conductance data for compounds.

conc. M	Temp. K	Molar Conductance (Λ) mol^{-1} cm^2 ohm^{-1} Compound 1	Compound 2	Compound 3	Compound 4
0.0030	283.15	0.917	0.577	0.517	0.280
	288.15	1.012	0.677	0.593	0.347
	293.15	1.230	0.787	0.627	0.447
	298.15	1.250	0.833	0.680	0.503
	303.15	1.400	1.030	0.713	0.663
	308.15	1.483	1.123	0.807	0.720
	313.15	1.850	1.167	1.033	0.817
	318.15	1.917	1.477	1.117	0.980
0.0015	283.15	1.220	0.620	0.553	0.287
	288.15	1.282	0.787	0.720	0.387
	293.15	1.353	0.933	0.893	0.473
	298.15	1.467	1.000	0.920	0.527
	303.15	1.613	1.160	0.947	0.793
	308.15	1.700	1.380	0.990	0.947
	313.15	2.000	1.533	1.100	1.067
	318.15	2.212	1.730	1.167	1.103
0.0008	283.15	1.270	0.667	0.587	0.467
	288.15	1.372	0.840	0.760	0.607
	293.15	1.470	1.067	0.960	0.693
	298.15	1.747	1.333	1.147	0.800
	303.15	1.920	1.520	1.213	1.120
	308.15	2.227	1.693	1.333	1.293
	313.15	2.400	2.133	1.467	1.403
	318.15	2.520	2.200	1.667	1.633
0.0004	283.15	1.523	0.880	0.683	0.587
	288.15	2.347	1.013	0.880	0.720
	293.15	2.573	1.173	1.073	0.800
	298.15	3.013	1.600	1.280	0.960
	303.15	3.467	1.840	1.340	1.307
	308.15	3.653	2.133	1.547	1.407
	313.15	3.733	2.533	1.680	1.593
	318.15	3.920	2.720	1.973	1.867
0.0002	283.15	1.607	0.963	0.695	0.607
	288.15	2.667	1.027	0.963	0.767
	293.15	2.855	1.235	1.103	0.833
	298.15	3.497	1.865	1.390	0.997
	303.15	3.849	1.998	1.497	1.333
	308.15	4.016	2.303	1.711	1.633
	313.15	4.230	2.763	1.925	1.700
	318.15	4.385	2.941	2.096	2.000

Table 2. Best fit results for compound-1.

	Fuoss-Hsia Modified					Fuoss-Hsia Complete				
Temp. K	K_d /10^{-4}	Λ_o	S^2	σ	Walden Product	K_d /10^{-4}	Λ_o	S^2	σ	Walden Product
283.15	2.222	1.0	0.05	0.014142	2.182	2.381	1.23	0.45	0.304056	2.68386
288.15	1.587	1.3	0.04	0.021213	2.5467	1.923	1.40	0.32	0.39598	2.7426
293.15	1.190	1.9	0.03	0.028284	3.3611	1.408	2.0	0.27	0.431335	3.538
298.15	0.909	2.0	0.02	0.035355	3.214	1.111	2.3	0.07	0.572756	3.6961
303.15	0.714	2.7	0.01	0.042426	3.9663	0.909	3.3	0.17	0.502046	4.8477
308.15	0.606	3.0	0.05	0.014142	4.023	0.800	4.0	0.88	0	5.364
313.15	0.508	4.7	0.02	0.035355	5.7904	0.667	4.5	0.33	0.388909	6.0368
318.15	0.357	6.0	0.07	0	6.822	0.556	7.0	0.07	0.572756	7.959

Table 3. Best fit results for compound-2.

	Fuoss-Hsia Modified					Fuoss-Hsia Complete				
Temp. K	K_d /10^{-5}	Λ_o	S^2	σ	Walden Product	K_d /10^{-5}	Λ_o	S^2	σ	Walden Product
283.15	0.649	1.1000	0.24	0.141421	2.4002	2.273	1.3000	0.22	0.438406	2.8366
288.15	0.556	1.3000	0.16	0.19799	2.5467	2.128	1.4000	0.17	0.473762	2.7426
293.15	0.417	1.4000	0.08	0.254558	2.4766	1.961	1.7000	0.84	0	3.0073
298.15	0.333	1.7000	0.44	0	2.7319	1.802	1.9000	0.57	0.190919	3.0533
303.15	0.286	1.8000	0.21	0.162635	2.6442	1.695	2.0000	0.38	0.325269	2.938
308.15	0.250	4.0000	0.24	0.141421	5.364	1.613	4.2000	0.75	0.06364	5.6322
313.15	0.218	5.0000	0.17	0.190919	6.16	1.538	5.3000	0.16	0.480833	6.5296
318.15	0.185	7.0000	0.04	0.282843	7.959	1.449	8.8000	0.26	0.410122	10.0056

Table 4. Best fit results for compound-3.

	Fuoss-Hsia Modified					Fuoss-Hsia Complete				
Temp. K	K_d /10^{-6}	Λ_o	S^2	σ	Walden Product	K_d /10^{-6}	Λ_o	S^2	σ	Walden Product
283.15	0.385	1.3000	0.1300	0.537401	2.8366	0.508	1.5000	0.1100	0.360624	3.273
288.15	0.370	2.0000	0.5400	0.247487	3.918	0.485	2.4000	0.6200	0	4.7016
293.15	0.351	2.6000	0.0100	0.622254	4.5994	0.452	3.2000	0.4000	0.155563	5.6608
298.15	0.333	3.0000	0.2000	0.487904	4.821	0.432	3.6000	0.3000	0.226274	5.7852
303.15	0.318	3.5000	0.8900	0	5.1415	0.419	4.4000	0.2100	0.289914	6.4636
308.15	0.305	4.0000	0.1400	0.53033	5.364	0.403	5.0000	0.4800	0.098995	6.705

Continued

313. 15	0.294	6.6000	0.1200	0.544472	8.1312	0.390	7.2000	0.1100	0.360624	8.8704
318.15	0.286	9.7000	0.1100	0.551543	11.0289	0.378	10.2000	0.3000	0.226274	11.5974

Table 5. Best fit results for compound-4.

	Fuoss-Hsia Modified					Fuoss-Hsia Complete				
Temp. K	K_d /10^{-3}	Λ_o	S^2	σ	Walden Product	K_d /10^{-3}	Λ_o	S^2	σ	Walden Product
283.15	0.244	1.5000	0.0200	0.388909	1.09	1.670	1.8000	0.0030	0.358503	2.18
288.15	0.200	2.2000	0.1000	0.33234	1.18	1.250	2.7000	0.1000	0.289914	7.84
293.15	0.161	3.0000	0.0500	0.367696	1.42	0.950	3.8000	0.0400	0.33234	8.85
298.15	0.122	3.5000	0.5000	0.049497	1.61	0.769	4.5000	0.0900	0.296985	11.20
303.15	0.099	4.1000	0.1800	0.275772	1.62	0.625	5.0000	0.1100	0.282843	11.80
308.15	0.070	6.8000	0.2900	0.19799	1.88	0.500	7.8000	0.2600	0.176777	12.10
313.15	0.050	7.2000	0.5700	0	2.3	0.400	8.5000	0.5100	0	12.30
318.15	0.043	9.8000	0.1000	0.33234	11.0	0.333	11.1000	0.1000	0.289914	14.80

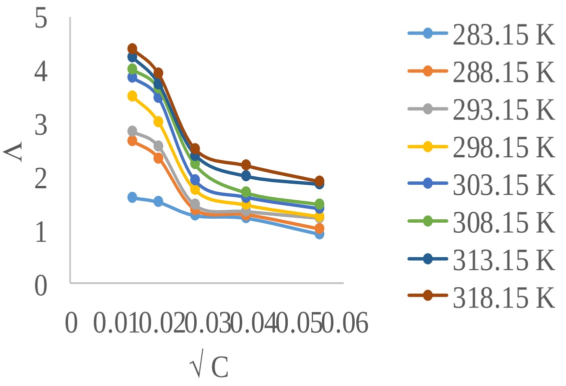


Figure 3. Molar conductance vs square root of concentration for compound 1 at different temperature.

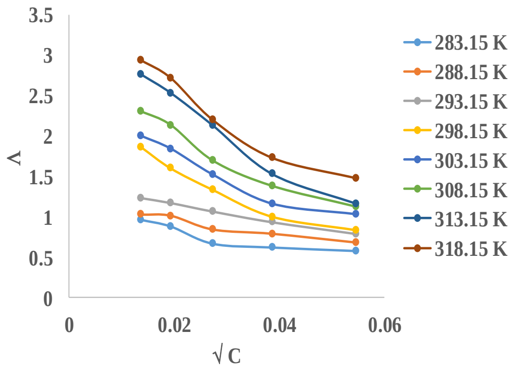


Figure 4. Molar conductance vs square root of concentration for compound 2 at different temperature.

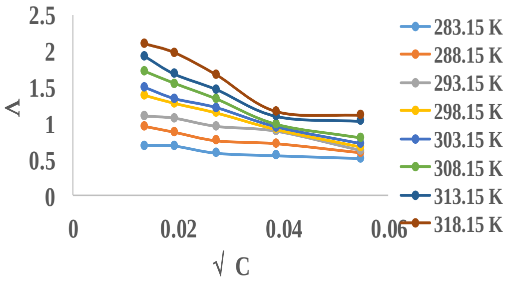


Figure 5. Molar conductance vs square root of concentration for compound 3 at different temperature.

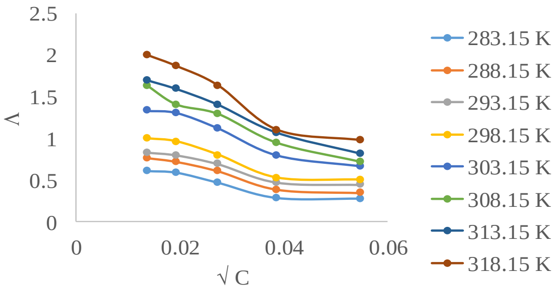


Figure 6. Molar conductance vs square root of concentration for compound 4 at different temperature.

The thermodynamic parameters for the dissociation reaction are obtained from temperature dependence of dissociation constant (Kd). The standard enthalpy (ΔH^o) is determined from slope of the logarithm (Kd) vs 1/T with (ΔG^o and ΔS^o). The slope is equal to ($-\Delta H/R$) to find Enthalpy, the intercept equal to ($\Delta S/R$) for finding entropy and then to calculate Gibbs free energy used [24, 25].

$$\Delta G=\Delta H-T\Delta S \qquad (5)$$

Walden product (previously known the product of viscosity (η) and conductivity at infinite dilution of a solution (Λo) it provides a measurement of the solvent-structuring activity of the solute) estimate as a function of temperature by:

$$\Lambda o(T)\ \eta(T) = \text{constant}. \qquad (6)$$

where $\eta(T)$ is a viscosity depends on temperature. The minimization of Λo and K_d values of complete and modified Fuoss-Hsia equations is estimated for compounds (1-3) then compared with compound 4 in 2-methoxy ethanol as a solvent. The results show that the increase of alkyl group chain leads to the decrease of the conductivity. The kinetics (osmotic) terms contributed to the increase in velocity of the ion. It is obvious from the minimization technique that the parameter Λo is expected to have the greatest effect on the values of S^2 during the variation of the two parameters K_d and Λo. Thus, Λo is the leading term in all the conductance equations. However, Λo is relatively insensitive to the values of K_d at the corresponding of minimum of S^2. Dissociation constants that are given in Tables (2, 3, 4 and 5) at different temperatures can therefore anticipate that these compounds do not behave as strong electrolyte and that their dissociations are far from complete. It can observe ion-pair (IP) or solvent separate ion pair (SSIP) formation according to the quantitative conductance data.For understanding the thermodynamic of the dissociation reactions it is useful to consider the enthalpic and entropic contribution to these dissociation and Gibbs free energy. This proves that dissociation for compound is true for compared (as showed in appendix). The standard enthalpy, free energy and entropy changes are determined by using [23] at different temperatures. The summary at this point gives the conductometric dissociation constant K_d to determine the standard free energy change for the postulated equilibrium. This opens the way to search for correlation between ΔG^o, ΔH^o and ΔS^o on the one hand , and to solutes and solvents on the other hand. According to minimization technique used here, the best K_d and Λ_o show an expected trend with temperature. Tables 2, 3, 4 and 5 clearly shows the temperature dependence of the Λ_o value. The increase of temperature leads to the increase of Λ_o and decrease of K_d, as a consequence the association of the compounds increases. As it is mentioned above, there is no literature value of Kohlrausch's law (independent migration of ions) for compounds 1, 2, 3 and 4 compared with the practical finding of Λ_o, therefore the formed results calculated based on statistical S^2. The above Figures from 7, 8, 9 and 10 show the good agreement for the thermodynamic parameters.

Table 6. Thermodynamic data for compound 1 using both equations.

Temperature K	Fuoss-Hsia Modified			Fuoss-Hsia Complete		
	$-\Delta H^o$ kJ mol^{-1}	ΔG^o kJ mol^{-1}	$-\Delta S^o$ J K^{-1} mol^{-1}	$-\Delta H^o$ kJ mol^{-1}	ΔG^o kJ mol^{-1}	$-\Delta S^o$ J K^{-1} mol^{-1}
283.15	4.661	52.57	201.4	3.378	47.06	179.4
288.15		53.57			47.96	
293.15		54.58			48.85	
298.15		55.59			49.75	
303.15		56.59			50.65	
308.15		57.60			51.54	
313.15		58.61			52.44	
318.15		59.61			53.34	

Table 7. Thermodynamic data for compound 2 using both equations.

Temperature K	Fuoss-Hsia Modified			Fuoss-Hsia Complete		
	$-\Delta H^o$ kJ mol^{-1}	ΔG^o kJ mol^{-1}	$-\Delta S^o$ J K^{-1} mol^{-1}	$-\Delta H^o$ kJ mol^{-1}	ΔG^o kJ mol^{-1}	$-\Delta S^o$ J K^{-1} mol^{-1}
283.15	3.260	52.01	195.2	1.166	33.72	123.2
288.15		52.99			34.33	
293.15		53.96			34.95	
298.15		54.94			35.57	
303.15		55.91			36.18	
8.15		56.89			36.80	
313.15		57.87			37.41	
318.15		58.84			38.03	

Table 8. Thermodynamic data for compound 3 using both equations.

Temperature K	Fuoss-Hsia Modified			Fuoss-Hsia Complete		
	$-\Delta H^o$ kJ mol^{-1}	ΔG^o kJ mol^{-1}	$-\Delta S^o$ J K^{-1} mol^{-1}	$-\Delta H^o$ kJ mol^{-1}	ΔG^o kJ mol^{-1}	$-\Delta S^o$ J K^{-1} mol^{-1}
283.15	0.750	40.39	145.3	0.748	39.72	142.9
288.15		41.12			40.44	
293.15		41.84			41.15	
298.15		42.57			41.86	
303.15		43.30			42.58	
308.15		44.02			43.29	
313.15		44.75			44.01	
318.15		45.48			44.72	

Generally, the thermodynamic functions (ΔH give information about energy, ΔS give information about disorder in given system and (ΔG give information about spontaneous in the forward and backward directions and equilibrium in this case may be positive or negative depending on temperature). The good agreement for the Walden product is the interpretation of the high viscosity of the medium [17, 26] while the K_d and Λ_o are showing the direct proportional sign minimization technique depending on the sum squire (S^2) or standard deviation (σ) which is a different between theoretical and practical values. However, the thermodynamic parameters are given good results about the interpretation between solute and solvent in non-aqueous solvent. Concerning the ΔH, it is determined from the slope of lnKd versus 1/T as shown in Figures (7, 8, 9 and 10) in which the negative values of enthalpy reflects weak interaction between cation and anion for all compounds. Therefore, the solvation is weak.

Table 9. Thermodynamic data for compound 4 using both equations.

Temperature K	Fuoss-Hsia Modified -ΔH° kJ mol^{-1}	Fuoss-Hsia Modified ΔG° kJ mol^{-1}	Fuoss-Hsia Modified -ΔS° J K^{-1} mol^{-1}	Fuoss-Hsia Complete -ΔH° kJ mol^{-1}	Fuoss-Hsia Complete ΔG° kJ mol^{-1}	Fuoss-Hsia Complete -ΔS° J K^{-1} mol^{-1}
283.15	4.670	53.49	205.4	4.107	45.16	199.0
288.15		54.52			46.03	
293.15		55.55			46.90	
298.15		56.57			47.77	
303.15		57.60			48.64	
308.15		58.63			49.51	
313.15		59.66			50.38	
318.15		60.68			51.25	

The existence of intermolecular hydrogen bonding between –OH group with oxygen atom of –COOH group in compound-1 restricts the ionization of hydroxyl group, which leads to the decrease in conductivity.

The ΔS decreases by the increase of temperature due to different changes between solute and solvent, or may be the consequence of attribution to formation of ion-pair or solvent separated ion pair interactions. The negative value of entropy is never spontaneous and the effect is produced by the charge species (ion and ion-pair) on the neighbored solvent molecules and its usefulness in investigating the media properties. However, ΔH and ΔS values proves the useful structural information of solute species and solute-solvent interaction [17]; therefore the entropy asserts that the investigating of media, and the negative value of entropy is important for the opposite effect produced by charge species (ion, IP, SSIP) on the neighbor solvent molecule. For the Gibbs, free energy values are never shown spontaneous reaction as they are observed in the solute and solvent interaction for the all compound compared with compound 4, i.e. the reaction needs temperature, stirring or pressure for the complex reaction to happen. The Walden product depends on temperature showed that the information could be obtained on ion solvent interactions as they are stated in Tables (2, 3, 4 and 5). The dissociation constant sequences of the compounds (1, 2, 3, and 4) are illustrated below:

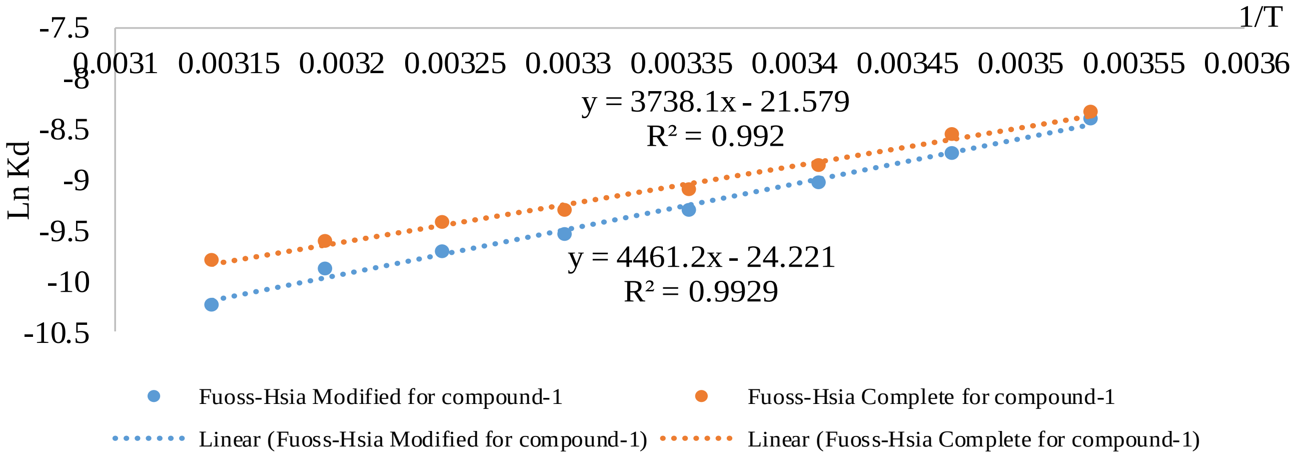


Figure 7. logarithm dissociation constant vs inverse temperature for compound 1.

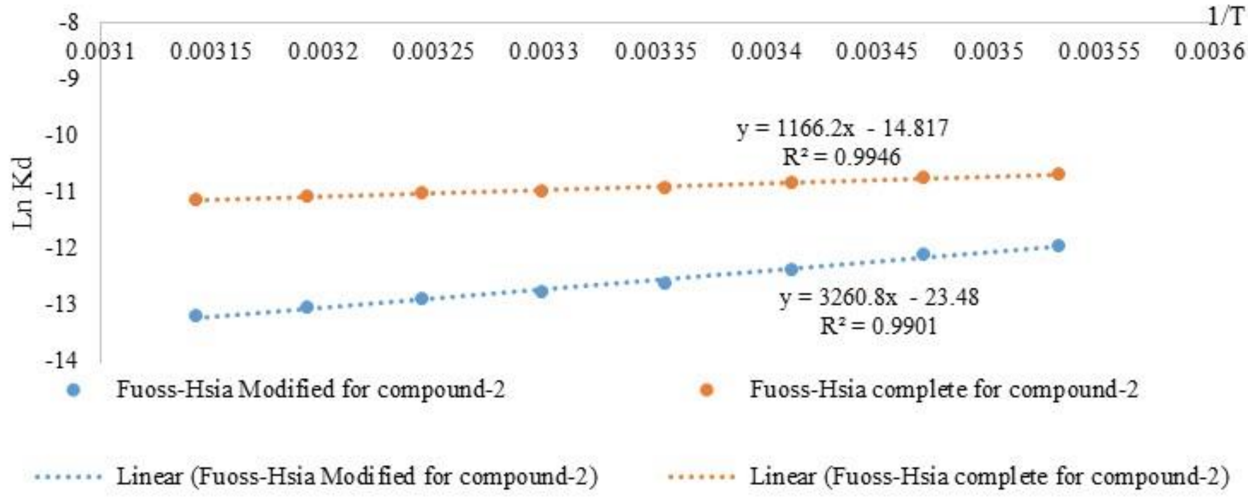


Figure 8. logarithm dissociation constant vs inverse temperature for compound 2.

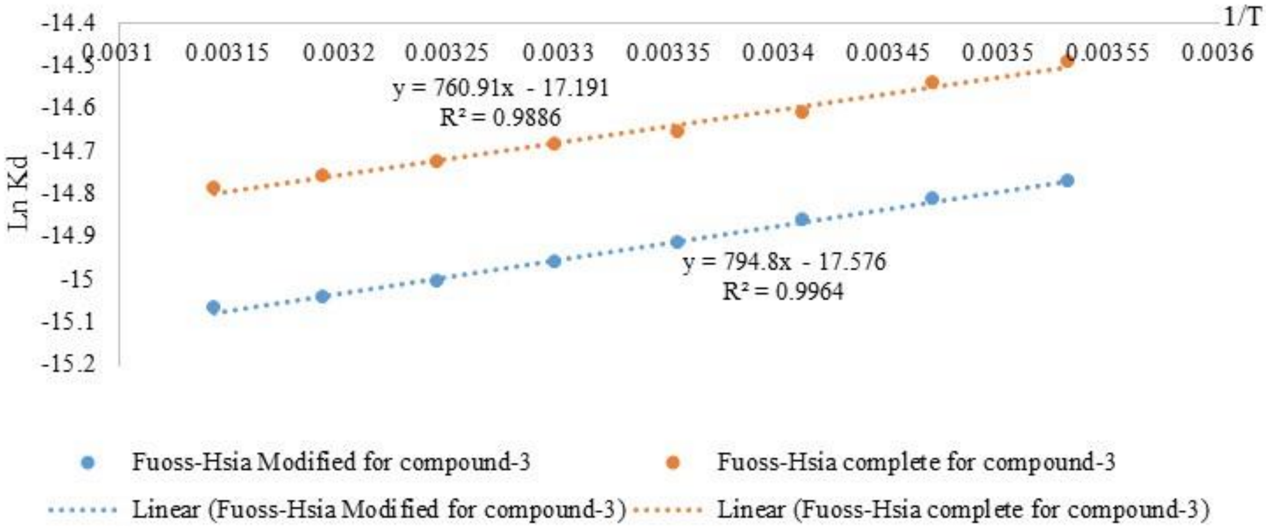


Figure 9. logarithm dissociation constant vs inverse temperature for compound 3

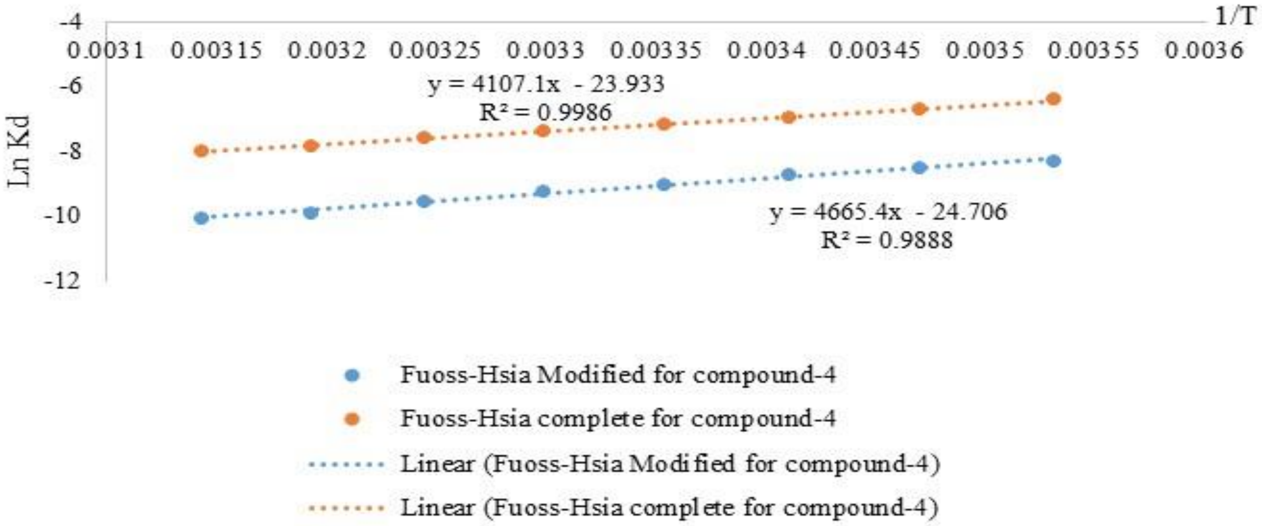


Figure 10. logarithm dissociation constant vs inverse temperature for compound 4.

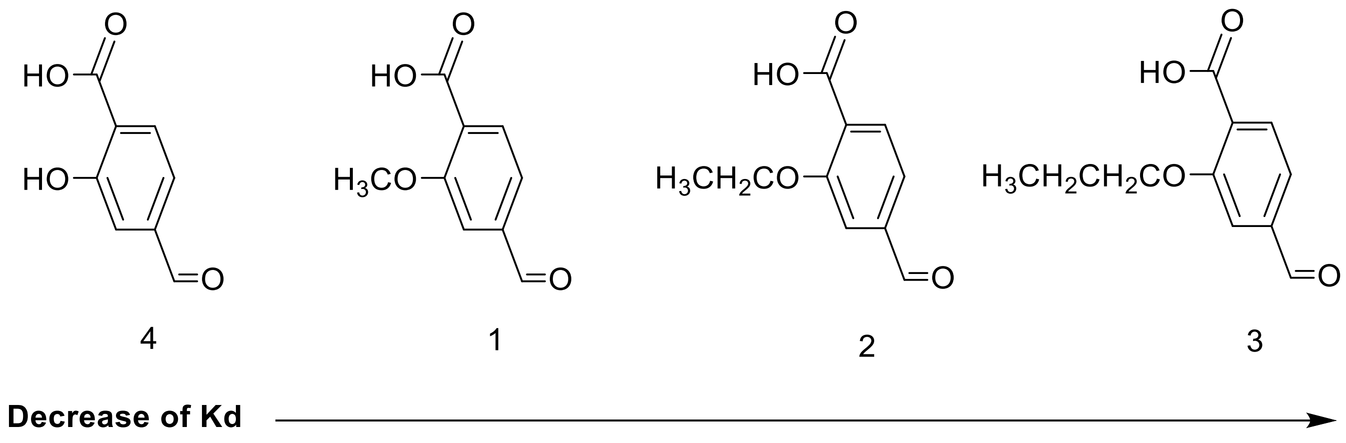


Figure 11. K_d scal for all compounds.

Both -OCH_3 and -OH groups have exhibited two effects on the aromatic ring: (1) Electron donates resonance or mesomeric effect (+M), and (2) Electron withdraws inductive effect (-I). For both acids, the electron withdrawing inductive effect (-I) is almost the same since both -OCH_3 and -OH groups are 4 carbons away from the acid center. However, when -OH group is attached to ortho-position, it has a more tendency to delocalize its lone pair electrons towards the aromatic ring than that of -OCH_3 group (Order of activating: -O–> -OH> -OCH_3). As a result, the electron density on the carbon ortho to –OH substitution group increases more than that on the carbon ortho to -OCH_3 substitution group. Another explanation, due to steric reasons, the C(benzene)−O−C(alkyl group) bond angle of

OCH_3 is going to be more than the C(benzene)−O−H bond angle of the -OH. Hence, the percent s-character is going to go up for the central oxygen atom in OCH_3 relatively (to rationalize this, think of the bond angles associated with sp3, sp2 and sp hybridization and their respective s-characters). Due to increased s-character on both sides of the OCH_3 oxygen, it can achieve an overall more electronegative substituent for the ring compared to OH, as the electrons displaced towards the oxygen from the methyl in OCH_3 in which it would still experience a lowering in the energy of the σ(O−CH_3) bond. Hence, as compared to OH, the ring will be activated less by OCH_3. The steric effect also plays a role within the different chain length alkoxy compounds, as a result thee dissociation order is (-OCH_3> - OCH_2-CH_3> - OCH_2-CH_2-CH_3) see Figure 11.

4. Conclusion

In conclusion, compounds of 1, 2, 3 are analyzed and compared with compound 4 with the use of conductometric methods in 2-methoxy ethanol as a solvent at different temperatures ranged between 283.15K-318.15K, evaluated by audio frequency conductance using both Fuoss-Hsia equations (modified and complete). A minimization technique is used here to estimate dissociation constant and molar conductance at infinity dilution with different temperatures. When the Λ_0 increases, the dissociation decreases at increased temperature, due to more ions formation in a solution, and greater conductance is reached. In addition of that, it was clearly observed that (CIP and SSIP) have their impact on conductivity. The Walden product also substantially increases with temperature. Finally, the standard thermodynamic parameters have been calculated deriving from mentioned temperature depending on dissociation constant, the thermodynamic functions (ΔG^o, ΔH^o and ΔS^o) showed a good indication on solute-solvent interaction. It was also concluded that mesomeric effect and the inductive effect also have their role on this study.

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Nomenclature

-OCH_3	Methoxy group,
-OCH_2-CH_3	Methoxymethane
-OCH_2-CH_2-CH_3	Methoxyethane
-OH	Hydroxyl group
-COOH	Carboxyl acid group)
Λ	Molar conductance (S m^2 mol^{-1})
Λ_0	Molar conductance in the limit of zero concentration
K	Coefficient related to the stoichiometry of the electrolyte
C	Concentration of the electrolyte (mEq/L)
E	Constant factor,
Jc	Long-range interaction
$K_A\Lambda_{0c}$	Pair formation near in concentration
H^+	Proton
Kd	Dissociation constants (M)
KA	KMAX in steps of DKA
L0	L0MAX in steps of DL0
η	Viscosity of solvent ($kg\cdot m^{-1}\cdot s^{-1}$)
D	Dielectrically constant of solvent
T	Absolute temperature (K)
Z	Valence of electrolyte
K_A	Initial K_A value
N	C_i/Λ_i pair numbers
C	(I, J) (N pairs of C and Λ data)
ΔH^o	Standard enthalpy (kJ mol^{-1})
ΔG^o	Gibbs free energy (J or KL)
ΔS^o	Standard entropy (J/K·mol)

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