

Short Communication

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THERMODYNAMICS OF IONIZATION PROCESS OF SOME WEAK ACIDS IN AQUEOUS SOLUTIONS

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INTRODUCTION

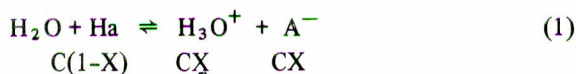
The ionization constant of weak acids are determined using different techniques [1-4]. The values of the ionization constants in aqueous solution of formic [5], acetic [6,7] chloroacetic [8], and propionic [9] acids are among the early investigated acids. The conductance technique is an accurate methods for determining the ionization constants of a weak acid [4,10].

In this investigation conductance measurements were carried out to study the effect of methylene group (-CH₂-) on the ionization process on a series of weak acids, namely; formic, acetic, propionic and butyric acids. It is worthnoting that the available data on such systems are neither systematic nor carried out using the same technique under similar conditions to allow fair and good comparison, hence rather scattered and not comparable.

The measurements were carried out with conductivity meter, model LBR, equipped with cell model LTA 100. Temperature was maintained constant by circulating water in the cell compartment at temperature $\pm 0.01^\circ$. Measurement carried out at 25, 30, 40 and 50^o for formic, acetic, propionic and butyric acid solutions of concentration range from 5×10^{-5} to 5×10^{-3} equivalent/l.

All acids used in this study were analytical reagent grade, and their solutions were made in deionized distilled water.

The ionization of a weak acid HA, expressed as:



where C is the concentration (equivalent/l), and X is the degree of ionization. The classical ionization constant, K_a, is expressed in term of equation (2)

$$K_a = \frac{\text{CX} \cdot \text{CX}}{\text{C}(1-\text{X})} = \frac{\text{CX}^2}{1-\text{X}} \quad (2)$$

The magnitude of K_a gives an indication of the extent of the ionization or the acid strength. Combining equation (2)

and the Arrhenius expression, $X = \Lambda / \Lambda_0$ (where Λ and Λ_0 are equivalent conductance and equivalent conductance at infinite dilution). We then obtain equation (3)

$$C \Lambda = K_a \Lambda_0^2 (1/\Lambda) - K_a \Lambda_0 \quad (3)$$

Plotting C Λ against 1/ Λ should yield a linear relationship, where K_a values can be calculated from the slope and the intercept.

The K_a values (Table 1) shows increase of ionization

Table 1. The values of K_a and PK_a at different temperatures for formic, acetic, propionic and butyric acids in aqueous solutions.

T (^o K)	Formic		Acetic		Propionic		Butyric	
	K _a .10 ⁵	PK _a	K _a .10 ⁵	PK _a	K _a .10 ⁵	PK _a	K _a .10 ⁵	PK _a
298	17.50	3.757	1.733	4.761	1.974	4.705	2.375	4.624
303	16.67	3.778	1.684	4.773	1.777	4.750	2.015	4.695
308	16.41	3.785	1.500	4.823	1.584	4.800	1.758	4.755
313	15.61	3.807	1.375	4.863	1.421	4.847	1.478	4.830
323	14.70	3.833	1.200	4.921	1.237	4.907	1.281	4.892

constant of formic acid when compared to acetic, propionic, and butyric acids. Replacing the nonacidic hydrogen of formic acid with a methyl group lowers the ionization constant by a factor of about ten. It appears then that the methyl group as well as other alkyl group is a slightly poorer electron withdrawer than the hydrogen atom. This acid weakening character is again in harmony with the thermodynamic data; ΔG° and ΔS° , (Table 2). The values

Table 2. Thermodynamic parameters for the ionization of formic, acetic, propionic and butyric acids in aqueous solutions.

	$-\Delta H^\circ$ K.cal/mol	$-\Delta G^\circ$ K.cal/mol	$-\Delta S^\circ$ cal/mol. ^o K
Formic acid	0,5663	5.39 \pm 0.27	19.19 \pm 0.10
Acetic "	1.3909	6.73 \pm 0.24	26.56 \pm 0.13
Propionic "	1.6408	6.83 \pm 0.42	27.28 \pm 0.25
Butyric "	2.2330	6.77 \pm 0.46	28.97 \pm 0.32

of ΔG° are all positive values and their magnitude increase as the number of methylene group increases. On the other hand, ΔS° have negative values and their magnitudes decrease as the number of methylene group increased. As general ΔH° have negative values, indicating that the ionization processes of all acids under investigation are exothermic. (Fig. 2) illustrates the relation between PK_a and T^{-1} .

If we now inspect the data in reference to the replacement of nonacidic hydrogen of $(\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH})$ with alkyl group of different number of methylene groups; CH_3- , CH_3-CH_2- , or $\text{CH}_3-\text{CH}_2-\text{CH}_2-$; namely; acetic, propionic, and butyric acids. The PK_a values decrease in the order :



Fig. 1 illustrates the relation between the PK_a values and the increase of the number of methylene group.

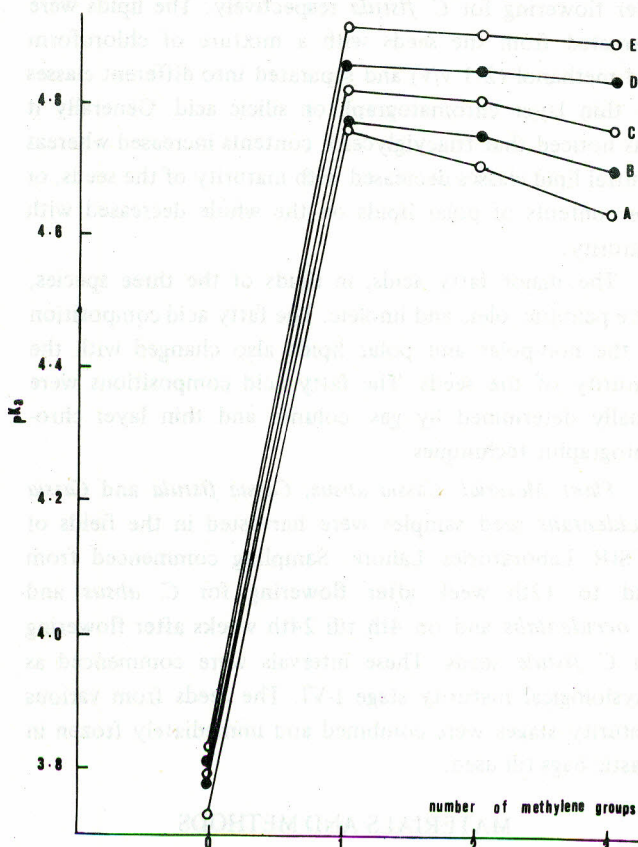


Fig. 1. pK_a vs number of methylene groups at (a) 25° (B) 30° (C) 35° (D) 40° and (E) 50°

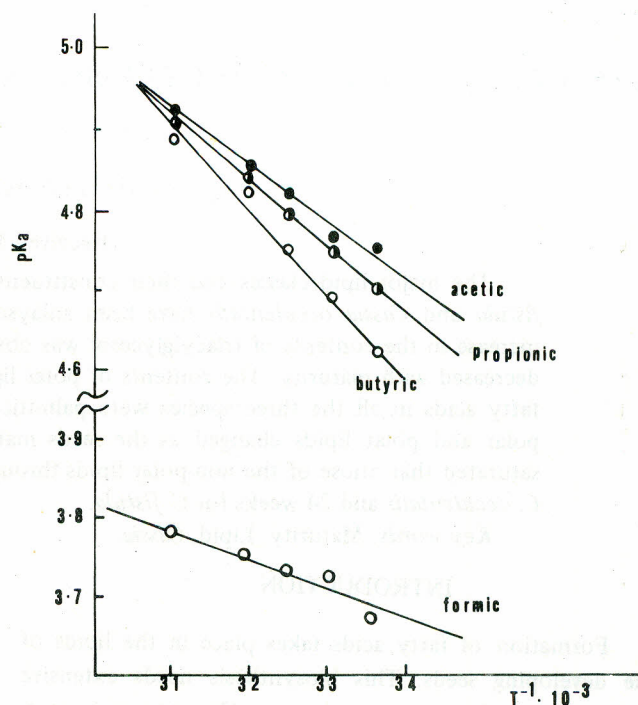


Fig. 2. PK_a vs T^{-1} for formic, acetic, propionic, and butyric acids.

Key words: Thermodynamics, Ionization of weak acids, Conductance.

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