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THERMODYNAMIC STUDIES ON THE IONIZATION PROCESS OF PROPIONIC ACID IN METHANOL-WATER MIXTURES

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The ionization processes of propionic acid in methanol-water mixtures at various temperatures were studied using conductometric technique. Propionic acid becomes less ionized as the proportion of methanol increases in the mixture, i.e., as the dielectric constant decreased. The results were reported in view of thermodynamic, where the ionization processes are exothermic ones. The conductance technique is one of the famous accurate methods for determining the ionization constants of a weak acid.

Key words: Conductance, Thermodynamics, Ionization.

INTRODUCTION

The ionization of carboxylic acids has been more extensively studied than has any other type of organic chemical equilibrium [1-5].

The ionization of propionic acid in aqueous medium has been discussed in our previous paper [6]. The present work deals with further studies on the ionization of propionic acid in mixed organic solvents; methanol-water mixtures, at various temperatures using conductometric technique. Methanol-water mixtures have lower dielectric constants as compared with that of pure water. The ionization of an acid decreases as the dielectric constant of the medium decreased, therefore, we shall discuss the effect of the dielectric constant on the ionization process of an acid.

The conductance technique is one of the most accurate methods for determining the ionization constants of a weak acids [7,8].

EXPERIMENTAL

Materials. Propionic acid used in this study was analytical reagent grade. Methanol was refluxed over magnesium metal and iodine for one hour, then purified by distillation at 65° (boiling point of methanol) in a water bath, deionized distilled water was used for the preparation of the solutions.

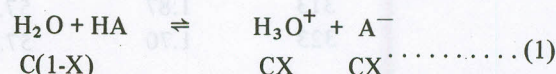
Apparatus. The measurements were carried out with a conductivity meter, model LBR, equipped with a cell model LTA 100. Temperature was maintained constant by circulating the cell compartment with water at the proper temperature $\pm 0.01^\circ$. Full details concerning electrical equipment and general technique have been outlined elsewhere [9].

Measurements were carried out for propionic acid in 10, 20 and 30 % methanol-water mixtures at 25, 30,

35, 40 and 50°. The conductance of propionic acid solutions has been measured in concentration range from 5×10^{-5} to 5×10^{-3} equivalent/L.

RESULT AND DISCUSSION

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].

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

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 and equivalent conductance at infinite dilution), we then obtain equation [3].

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

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

The K_a values which are calculated are tabulated in Table 1.

It is obvious that K_a values for propionic acid in methanol-water mixtures are lower than in pure water, i.e., propionic acid is more fully ionized in pure water than in methanol-water mixtures; its ionization involves a separation of charges and this is greatly facilitated in medium of higher dielectric constant.

Table 1. The values of K_a and pK_a for propionic acid in 10, 20, and 30% methanol-water mixtures at various temperatures.

% of methanol by weight	T (°K)	K_a (10^6)	pK_a (10)
10	298	3.26	54.87
	303	3.10	55.09
	308	2.99	55.23
	313	2.88	55.41
	323	2.65	55.77
20	298	2.83	55.48
	303	2.70	55.69
	308	2.57	55.90
	313	2.46	56.09
	323	2.23	56.52
30	298	2.30	56.38
	303	2.18	56.61
	308	2.02	56.95
	313	1.87	57.28
	323	1.70	57.69

Inspection of the data of Table 1, show that the ionization of propionic acid generally decreases steadily as the temperature is increased, but it decreased drastically with increasing proportion of the methanol in the mixtures. This in good agreement with the fact that methanol is a hydrogen bonded solvent (which is expected to be retarding the mobility of the ions and hence results in a decrease of the ionization of propionic acid). Therefore, as the proportion of methanol increase, the ionization of the acid decreased.

This acid weakening character is again in harmony with the thermodynamic data, ΔG° , ΔH° , and ΔS° which are tabulated in Table 2. Fig. 1, illustrate the relation between the logarithm of the ionization constants against the reciprocal of the temperatures.

The values of ΔG° are positive and their magnitudes increase with an increase in both temperature and proportion of methanol in mixtures.

As in general, ΔH° have negative values, indicating that the ionization processes of an acid are exothermic ones. The exothermicity increases as the proportion of methanol increase in the mixtures.

ΔS° have negative values and their magnitudes increase as the proportion of methanol increases in the mixtures.

The minus sign of ΔS° deals that the reaction tend to go spontaneously in the reverse direction, i.e., become less ionized, and as the proportional of methanol increase the values of ΔS° increased also, i.e., become more less ionized.

Table 2. Thermodynamic parameters for ionization process of propionic acid in methanol-water mixtures.

% of methanol by weight	T (°K)	$-\Delta H^\circ$ (K.J.mol ⁻¹)	ΔG° (K.J.mol ⁻¹)	$-\Delta S^\circ$ J(mol.°K) ⁻¹
10	298	2.88	31.30	114.70
	303	2.88	31.95	114.95
	308	2.88	32.56	115.06
	313	2.88	33.20	115.27
	323	2.88	34.48	115.67
20	298	3.29	31.65	117.25
	303	3.29	32.30	117.46
	308	3.29	32.96	117.69
	313	3.29	33.61	117.89
	323	3.29	34.95	118.39
30	298	4.19	32.16	121.98
	303	4.19	32.84	122.21
	308	4.19	33.58	122.63
	313	4.19	34.32	123.04
	323	4.19	35.67	123.41

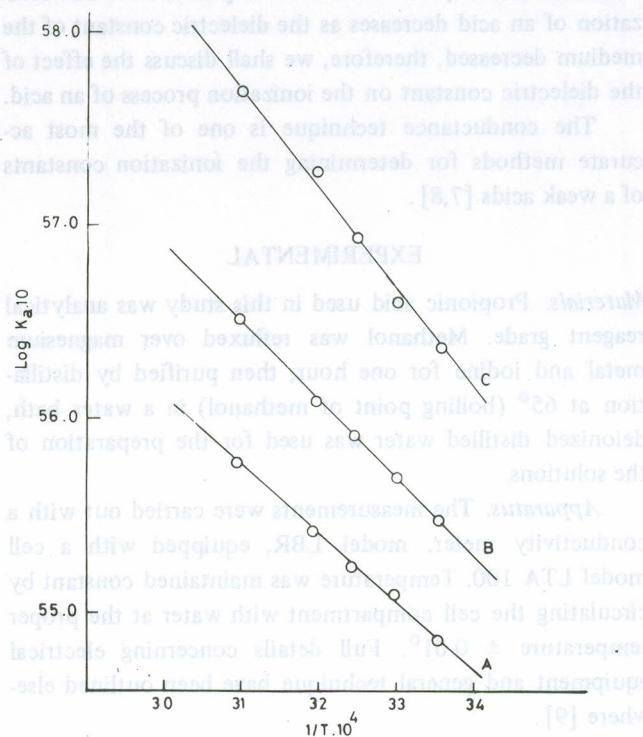


Fig. 1. $\log K_a$ vs $1/T$ for propionic acid in (A) 10 %, (B) 20 %, and (C) 30 % methanol-water mixtures.

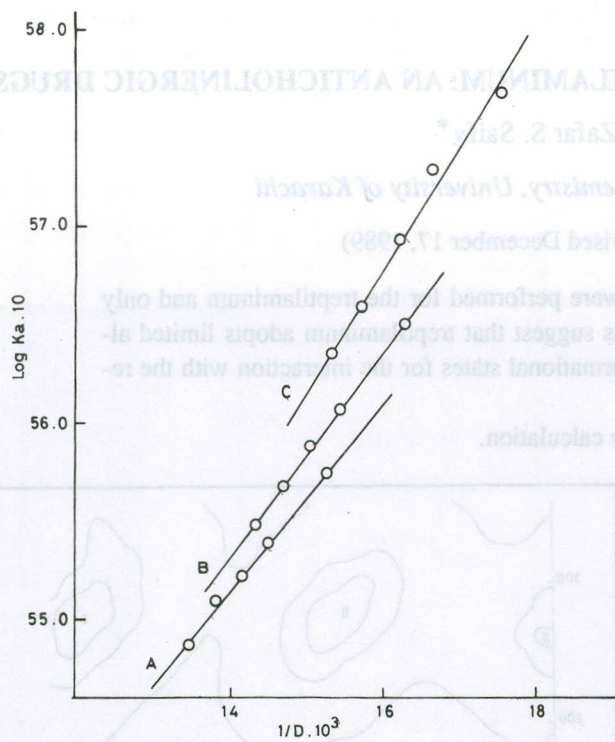


Fig. 2. P_{K_a} vs $1/D$ for propionic acid in (A) 10 %, (B) 20 %, and (C) 30 % methanol-water mixtures.

The dependence of P_{K_a} on the dielectric constant is shown in Fig. 2, where the minus logarithm of ionization constants is a linear function of the reciprocal dielectric constants for the different systems under investigation.

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Fig. 1. Energy contours for repulminium for the rings I, II.

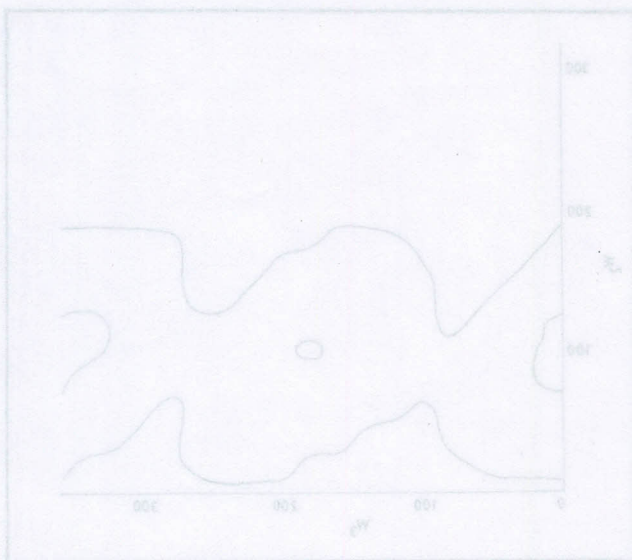


Fig. 2. Energy contours for repulminium for the rings I, II, III.

The present work describes the determination of repulminium (molecule A) and calculations of potential energy based on the Kohn-Sham method [2]. 3D computer Mark-M-88 was used throughout this work.

METHOD OF CALCULATION

The mathematical details have already been published by us [2,4] and Kohn-Sham [2] Fig. 3 shows the structure of repulminium and three parts of the structure are labeled as I, II, III. The rotation of ring I about C₁-C₂ the rotation of ring II about the bond C₁-C₂ and the rotation of ring III about the bond C₁-C₂ can be designated as W₁, W₂ and W₃ respectively.

The positions of atoms in rings I, II, III can be calculated by rotating ring I about C₁-C₂, ring II about C₁-C₂ and ring III about C₁-C₂. As a first step the conformation of ring I and ring II are determined. The pairs of atoms selected are C₁-C₂, C₃-C₄, C₅-C₆, C₇-C₈, C₉-C₁₀, C₁₁-C₁₂, C₁₃-C₁₄, C₁₅-C₁₆, C₁₇-C₁₈, C₁₉-C₂₀, C₂₁-C₂₂, C₂₃-C₂₄, C₂₅-C₂₆, C₂₇-C₂₈, C₂₉-C₃₀, C₃₁-C₃₂, C₃₃-C₃₄, C₃₅-C₃₆, C₃₇-C₃₈, C₃₉-C₄₀, C₄₁-C₄₂, C₄₃-C₄₄, C₄₅-C₄₆, C₄₇-C₄₈, C₄₉-C₅₀, C₅₁-C₅₂, C₅₃-C₅₄, C₅₅-C₅₆, C₅₇-C₅₈, C₅₉-C₆₀, C₆₁-C₆₂, C₆₃-C₆₄, C₆₅-C₆₆, C₆₇-C₆₈, C₆₉-C₇₀, C₇₁-C₇₂, C₇₃-C₇₄, C₇₅-C₇₆, C₇₇-C₇₈, C₇₉-C₈₀, C₈₁-C₈₂, C₈₃-C₈₄, C₈₅-C₈₆, C₈₇-C₈₈, C₈₉-C₉₀, C₉₁-C₉₂, C₉₃-C₉₄, C₉₅-C₉₆, C₉₇-C₉₈, C₉₉-C₁₀₀.

RESULTS AND DISCUSSION

Conformational maps for the parts I, II and III are given in (Fig. 1) and (Fig. 2) respectively. The contour map