Acid Dissociation Constants of Some Maleamic Acids In Ethanol and Dioxane - Water Mixtures

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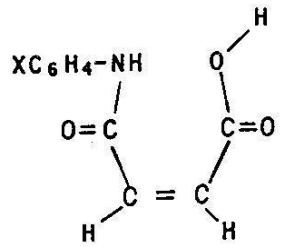
Summary: Values of the dissociation constants pK_{HA} of a number of monosubstituted maleamic acids were determined potentiometrically using the glass electrode and spectrometrically in various mole fractions of ethanol - and dioxane - water mixtures. The resulting Hammett plots of pK_{HA} Vs σ were found linear in these solvent mixtures. The same ρ_{HA} values - 0.61 ± 0.1 were found in the same solvent mixtures.

Introduction

When studying the acid dissociation constants, pK_{HA}, of an organic acid which is sparingly soluble in water, it may be expedient to measure its magnitude in a series of dioxane-water mixtures and extrapolate the values to zero mole fraction of dioxane. This procedure proved successful with dithizone [1]. An approximate relationship was found between the measured pKa values of water, formic acid, acetic acid and propionic acid and the mole fraction of dioxane [2], in the aqueous solvent mixtures. Van Uitrit and Hass reported a similar behaviour for β-diketones [3]. It is now apparent to correlate the pH-meter readings with the actual concentration or activity of the hydrogen ions in aqueous dioxan. A calibration curve should be obtained in reference to the mole fraction of dioxane, the total electrolyte concentration and the temperature used.

Considering the abundance of using maleamic acid as drugs or in polymer synthesis [4], it is surprising that nothing has been reported in the literature corresponding to the behaviour of such compounds (Ia-e) at different pH values in aqueous-organic solvent mixtures.

This paper reports the results of potentiometric and spectrophotometric studies of several monosubstituted maleamic acids (Ia-e) at various pH values in mixed ethanol and dioxane-water mixtures.



X=a=H b=p-Cl c=p-CH_3 d=p-OCH_3 e=p-NO_2

Experimental

Materials:

Ethanol and dioxane were purified, stored and dispensed as described elsewhere [5]. Maleamic acid derivatives were prepared previously [6]. Other chemicals used were of analytical or reagent grade quality.

Table-1
Ionisation constants pK_1 of some maleamic acids at various mole fraction of water - ethanol and dioxane at 25.0 ± 0.1°C

Compound	Ionisation constants pK_1				pK_o
	Ethanol (n)		Dioxane (n)		water
I_a	6.00	(0.09)	4.80	(0.05)	4.55
	6.45	(0.21)	5.00	(0.075)	
	6.05	(0.375)	5.40	(0.12)	
	6.90	(0.54)	5.54	(0.19)	
I_b	3.60		3.50		3.33
	4.05		3.70		
	4.76		3.40		
	5.45		4.35		
I_c	5.90		5.20		5.60
	6.40		5.40		
	6.90		5.80		
	7.70		6.05		
I_d	6.40		5.60		5.70
	6.86		5.75		
	2.30		6.05		
	8.05		6.50		
	2.95		3.70		
I_e	4.35		4.00		3.50
	5.05		4.20		
	5.85		4.50		

(n) mole fraction

The pH measurements were made using an onion pH-meter. All measurements were made at 25 ± 0.05°C.

The pKa determinations were made potentiometrically by titrating 50 ml 10^{-3}M maleamic acid in 50% v/v ethanol or dioxane-water mixture with 0.01M NaOH and measuring the pH after each addition. PKa_1 was calculated for each measurements using the relation

$$pKa_1 = pH + \log_{10}\frac{[HC] + [OH^-]}{[C^-] - [OH]} + A$$

HC and C represent the nonionized and ionized maleamic acid respectively. A, the activity correction was calculated according to Van Uitret [3].

The second dissociation constants, pKa_2, were determined spectrophotometrically, by measuring the absorbances of 10^{-5}M of the acid in 50% v/v ethanol or dioxane-water media at various pH. The spectra of the compounds investigated were obtained at 25 + 0.05°C by using Sp Pye Unicam 1800 spectrophotometer.

Table-2
Ionisation constants pK_2 of some maleamic acids at various mole fraction of water - ethanol and dioxane at 25.0 ± 0.1°C

Compound	Ionisation constants pK_2				pK_o water
	Ethanol (n)		Dioxane (n)		
I_a	10.11	(0.09)	10.20	(0.05)	9.95
	10.33	(0.21)	10.32	(0.075)	
	10.70	(0.375)	10.52	(0.120)	
	11.02	(0.540)	10.31	(0.190)	
I_b	9.82		9.97		9.70
	10.03		----		
	10.40		10.29		
	10.73		10.58		
I_c	10.19		10.32		10.05
	10.41		10.49		
	10.72		10.52		
	11.04		11.99		
I_d	10.31		10.42		10.15
	10.52		10.54		
	10.83		10.82		
	11.22		11.11		
I_e	9.40		10.01		9.81
	10.12		10.13		
	10.49		10.32		
	10.31		10.61		

(n) mole fraction

Results and Discussion

Potentiometric determination of pK_1.

The dissociation constants determined for maleamic acids (Ia-e) namely pK_1 for the neutralization of the carboxylic group as a function of solvent. Composition are listed in (table I).

Values of pK_1 were determined from pH measurements in aqueous solutions of different mole fractions of ethanol and dioxane.

Usually, equation (1) is used for such conditions.

$$-\log H^+ = \beta + \log \mu H^\circ + \lg \pm \gamma \quad (1)$$

where B = actual pH meter readings

μH° = correction value appreciate to zero ionic strength

$\gamma \pm$ = mean activity coefficient

The extrapolation of the linear plots of pK_1 vs solvent composition (Fig.1) to zero mole fraction of the

organic solvent gives pK_o values which follow the equation

$$pK_o = pK_1 - bn \quad (2)$$

where pK_1 = acid dissociation constant at (n) mole fraction

and b = constant.

The evaluation of pK_2 potentiometrically, for the ionization of the amide hydrogen was unsuccessful and therefore abondoned.

Spectrophotometric determination of pK_2:

pK_2 values listed in table-2 are assigned to the ionization constants of the amide group in aqueous solutions of different mole fractions of ethanol and dioxane. pK_2 values were calculated from the spectra of maleamic acid solutions at various pH values.

Again pK_o values (table 2) for the amide group were determined using equation (2).

The dielectric dependence of pK_s at various solvent composition are shown in Fig.2. As observed the pK values are inversely proportional to the dielectric constant of the medium, indicating that the proton accepting ability of the medium decreases with the increase in the mole fraction of organic solvent.

In general the reaction constants decrease with the dielectric constant of the medium. Such a dependence is in accordance with the relation (3) observed

$$pK = (B_1/\varepsilon + B_2)\, RT/d^2 \quad (3)$$

where,

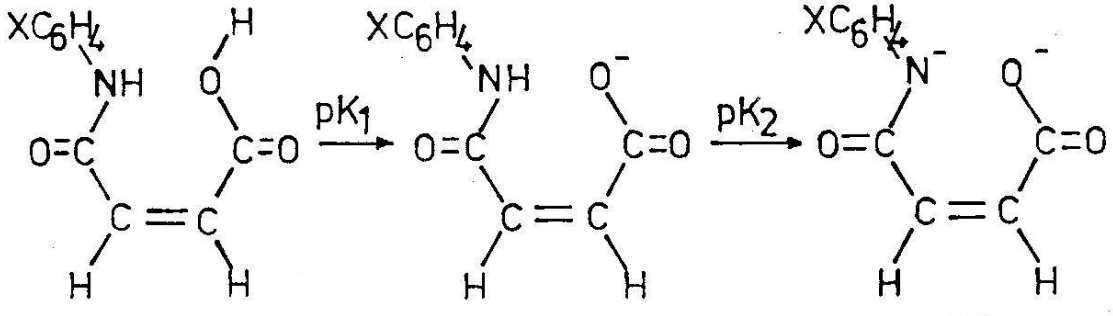
ε = dielectric constant

for the acid dissociation constants of phenol [7] and carboxylic acids [8].

Application of Hammett equation to the acid dissociation constants of the maleamic acids, linear relations are found in Figs.(3 & 4) with correlation value $\gamma = 0.995$. The reaction constant $\rho(0.86, 0.88)$ is higher in ethanol - and dioxane - water mixtures than in pure water $\rho(0.78)$.

The data in table (1 & 2) show that the acidity of the compounds studied depends on the nature of substituents on the anilide moiety of the molecule as well as the polarity of medium.

Consequently the ionization of maleamic acid can be reported by the following scheme.



I

a) X=H b) X=p-Cl

II

c) X=p-CH_3

III

d) X=p-OCH_3 e) X=p-NO_2

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