

Ionization Constants of Some Hydroxycoumarins in Dioxane-Water & Ethanol-Water Media

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The ionization constants (pK_a) of 8-amino-7-hydroxy-4-methylcoumarin (AHMCH) and 7-hydroxy-4-methylcoumarin-6-carboxylic acid (HMCCH₂) have been determined potentiometrically in 50% dioxane (v/v) and 50% ethanol (v/v) at various ionic strengths. The ionization constant of 7-hydroxy-4-methyl-6-nitrocoumarin (NHMCH) has been determined in 50% dioxane only due to its insolubility in ethanol. Thermodynamic dissociation constants (pK_a^T) have been obtained by extrapolation to zero ionic strength. The values of ΔG , ΔH and ΔS have also been calculated for the ionization process.

THE acid-base equilibria of hydroxycoumarin derivatives have not been studied much. Except for the work of Foffani *et al.*¹, Mattoo²⁻⁴, Adachi and Ejima⁵ and Manku⁶, no other work of any consequence is available. It was therefore of interest to determine the ionization constants of some hydroxy coumarin derivatives, viz., 8-amino-7-hydroxy-4-methylcoumarin (AHMCH), 7-hydroxy-4-methylcoumarin-6-carboxylic acid (HMCCH₂), 7-hydroxy-4-methyl-6-nitrocoumarin (NHMCH).

AHMCH, HMCCH₂ and NHMCH were prepared as described elsewhere⁷. The pK_a values were determined^{7,8} in 50% dioxane (v/v) and 50% ethanol (v/v) by the direct pH titration technique as described by Albert and Sarjeant⁸.

Most of the chemicals used were of analar (BDH) quality. NaClO₄·2H₂O (Reidel) was used for adjusting the ionic strength. Dioxane (Baker, USA) and ethanol were purified as described in literature⁹. Carbonate-free potassium hydroxide (BDH) was prepared according to Albert and Sarjeant⁸.

The pH measurements were made on a Beckman pH meter (model H2) using a glass-calomel electrode assembly.

For finding the thermodynamic ionization constants of these compounds, studies were carried out at 25° and at different ionic strengths viz. 0.05, 0.10, 0.15 and 0.20 and the results were extrapolated to zero ionic strength to obtain pK_a^T . For the determination of thermodynamic parameters, the studies were carried out at 15°, 25°, 35° and 45° and fixed ionic strength of 0.10.

Free energies of these reactions have been calculated using the equation $\Delta G = -RT \ln K = 2.303 T pK$. Plots of $\log K$ vs $1/T$ were linear and ΔH and ΔS values were calculated by using the usual expressions.

The pK_a values at different temperatures and the ΔG , ΔH and ΔS values are recorded in Table 1.

An examination of the data in Table 1 shows that HMCCH₂ ionizes in two steps, while AHMCH and NHMCH have only one ionization step. The two dissociation steps of HMCCH₂ are obviously due to the carboxylic acid group and the phenolic group. pK_1 of HMCCH₂ is due to the ionization of the —COOH group and pK_2 is due to the phenolic —OH. In the other two compounds the pK_1 are due to the phenolic —OH.

A comparison of pK 's in 50% dioxane, due to the phenolic hydroxyl shows that NHMCH is the strongest acid ($pK_2^T = 6.12$) and HMCCH₂ is the weakest ($pK_2^T = 10.42$). AHMCH has an intermediate value of pK_2^T (8.59).

NHMCH has a strong deactivating nitro group in position-6, which facilitates the release of the proton from —OH. Reverse is true for AHMCH, the —NH₂ at position-8 being an activating group, the O—H bond gets strengthened, and the release of the proton becomes more difficult. The pK_2^T of HMCCH₂ is due to a combination of factors. After the ionization of the carboxylic acid group, the molecule is negatively charged, and a second ionization destabilizes the molecule, due to the repulsive interaction between two adjacent negative charges. A more important factor is presumably the stabilization of the singly ionized acid by intramolecular hydrogen bonding.

The pK_a values of HMCCH₂ and AHMCH were also determined in 50% ethanol. NHMCH could not be studied in this medium as it was practically insoluble. The trend in 50% ethanol is the same as in 50% dioxane (cf. Table 1). An interesting point is that HMCCH₂ and AHMCH are slightly stronger acids in ethanol than in dioxane. The major reason seems to be the greater solvation of the acid anions in a polar solvent like 50% ethanol, than in a less polar solvent like 50% dioxane. It may also be noted that the dielectric constant of 50% ethanol is greater than that of 50% dioxane and this equally explains the lowering of pK_a from 50% dioxane to 50% ethanol, because charge separation is favoured by increased dielectric constant of the medium. It has been observed by Dewar¹⁰ in the case of keto-enol tautomerism that the more polar tautomer is always more stable in a more polar solvent, due to its greater solvation in that solvent. This mechanism seems to be applicable in the present case also, and this greater solvation is energetically more favourable to the acid anion than to the undissociated acid. In the case of pK_2 of HMCCH₂, apart from this solvation, there is a possibility of greater solvent —COO⁻ hydrogen bonding, which competes with the intramolecular H-bonding, significantly reducing the singly ionized acids stability in 50% ethanol in comparison to its stability in 50% dioxane. This destabilization probably makes the second ionization easier in 50% ethanol than in 50% dioxane.

The variation in pK_a with temperature (in dioxane) of all these compounds shows that an increase in temperature decreases the value of pK_a (cf. Table 1). This is normally observed¹¹ for most acids in the temperature range studied. The ΔG and ΔH values are positive and the ΔS values are negative.

TABLE 1 — IONIZATION CONSTANTS AND THERMODYNAMIC FUNCTIONS OF SOME HYDROXYCOUMARIN DERIVATIVES

Compound	Temp. °K	Ionization constant	(Ionic strength = 0.1)		ΔH^* kcal/mol	ΔS e.u.
			pK	ΔG kcal/mg		
50% DIOXANE						
HMCCH ₂	288.16	pK_1	4.60	6.07	5.040 ± 0.010	-3.548 ± 0.015
	288.16		4.47	6.10		
	308.16		4.35	6.13		
	318.16		4.23	6.16		
HMCCH ₂	288.16	pK_2	10.35	13.65	8.400 ± 0.010	-18.250 ± 0.012
	298.16		10.15	13.85		
	308.16		9.95	14.03		
	318.16		9.75	14.19		
AHMCH	288.16	pK_1	8.49	11.20	8.400 ± 0.015	-9.766 ± 0.10
	298.16		8.30	11.32		
	308.16		8.10	11.42		
	318.16		7.90	11.50		
NHMCH	288.16	pK_1	5.97	7.87	6.300 ± 0.015	-5.480 ± 0.02
	298.16		5.82	7.94		
	308.16		5.67	8.00		
	318.16		5.52	8.03		
50% ETHANOL						
HMCCH ₂	288.16	pK_1	4.25	5.61	5.050 ± 0.20	-1.947 ± 0.015
	298.16		4.12	5.62		
	308.16		4.00	5.64		
	318.16		3.88	5.65		
HMCCH ₂	288.16	pK_2	10.10	13.32	6.088 ± 0.10	-25.095 ± 0.015
	298.16		9.95	13.57		
	308.16		9.81	13.83		
	318.16		9.66	14.06		
AHMCH	288.16	pK_1	8.15	10.75	6.505 ± 0.015	-14.760 ± 0.020
	298.16		8.02	10.91		
	308.16		7.85	11.07		
	318.16		7.70	11.20		

NHMCH is not soluble in ethanol.
*Average values.

ΔH was assumed constant over the range of temperatures studied and was evaluated from the slope of the plot of pK_a vs $1/T$. From this average value of ΔH , ΔS was calculated using the standard relationship

$$\Delta G = \Delta H - T\Delta S$$

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Ion-Solvent Interaction in Propylene Carbonate from Conductivity Data

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Ion-solvent interaction of some tetraalkylammonium and common ions in propylene carbonate has been studied using electrolytic conductivity data and the derived Walden product. The R_4N^+ and halide ions do not appear to interact appreciably with the solvent but Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ ions are solvated.

THE ion-solvent interaction of tetraalkylammonium and Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ ions has