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Determination of pK_a values of azlactone dyes in non-aqueous media

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Abstract

4-Arylidene-2-aryl-5-oxazolone (azlactone) structures have wide range of applications arising from their promising photophysical and photochemical activities. Some of this class of dyes exhibit pH-dependent absorption and emission based response. For this reason, precise determination of the acidity constants (pK_a) of the azlactone derivatives is necessary for further studies in different media. In this study, five different azlactone derivatives were chosen to obtain pK_a values. The acidity constants were determined by using potentiometric titration method. The chosen derivatives were titrated with tetrabutylammonium hydroxide in solvents of dimethylformamide, *tert*-butanol, isopropanol, acetone and acetonitrile. A computerizable derivative method was used for a precise description of the end point and consequently the pK_a values. All compounds exhibited stoichiometric and well shaped potentiometric titration curves.

Keywords: Azlactone; Non-aqueous media titrations; Potentiometric method

1. Introduction

Azlactone derivatives have been synthesized and used by chemists in various applications resulting in the commercialisation of these products. Donor–acceptor type azlactone dyes are reported as "very brilliant" [1]. Orange-red and greenish yellow disperse dyes with CAS (Chemical Abstract Service) numbers of [25744-09-6] and [51202-86-9] have been intensely studied by chemists at Ciba and Badische Anilin Soda Fabrik (BASF), commercialised, and, used in polyesters as polymer additives [2,3]. They possess excellent colouring power and light fastness [4]. The azlactone derivative 4-(4′-methoxybenzylidene)-2-phenyloxazolin-5-one also appears as a novel nonlinear optical material which exhibits large powder SHG (Second Harmonic Generation) efficiency and sufficient transparency in the region of the second harmonic of Nd:YAG (Yttrium Aluminum Garnet) laser radiation [5]. In recent years, photophysical and photochemical properties of azlactone derivatives in crystalline state [6], sol–gel and PVC (Polyvinylchloride) matrices have been determined by spectroscopic techniques. Ertekin et al. used the azlactone derivative 4-(*p*-*N*,*N*-dimethylamino phenylmethylene)-2-phenyl-5-oxazolone as an effective pH indicator in immobilised form [7,8].

Besides the above mentioned applications, the knowledge of dissociation constants (pK_a's) of azlactones is of fundamental importance in order to provide information for scientists working on chemical reactivity, salt formation, chromatographic separations (especially estimation of retention times), selectivity and pH dependency of mobile phase.

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Conventional techniques for pK_a determination cover potentiometric, conductometric and spectrophotometric titrations with proper solvent–titrant combinations and instrumentation.

In this work five different azlactone derivatives namely:

4-phenylmethylene-2-phenyl-5-oxazolone; (**I**),
4-*o*-hydroxyphenylmethylene-2-phenyl-5-oxazolone; (**II**),
4-(*p*-*N*,*N*-dimethyamino phenylmethylene)-2-phenyl-5-oxazolone; (**III**),
4-(*p*-methoxyphenylmethylene)-2-phenyl-5-oxazolone; (**IV**),
4-(2-hydroxynaphthylmethylene)-2-phenyl-5-oxazolone; (**V**),

were titrated potentiometrically with tetrabutylammonium hydroxide (TBAOH) in solvents of dimethylformamide, *tert*-butanol, isopropanol, acetone and acetonitrile (Fig. 1). The half neutralization potentials (HNP) and pK_a values were determined by using a computerizable derivative method [9].

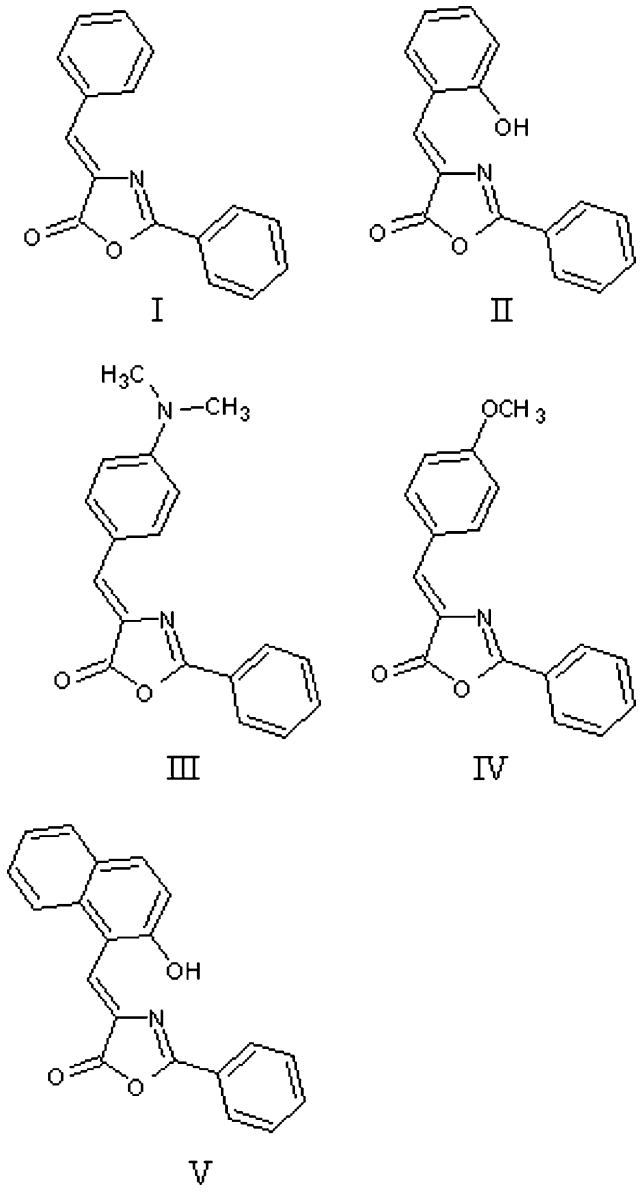

Fig. 1. Schematic structures of the potentiometrically titrated azlactone derivatives in different non-aqueous solvents.

2. Experimental

2.1. Reagents

0.1 N solution of tetrabutylammonium hydroxide (for titrations in non-aqueous media) was purchased from Merck and diluted with chromatographic grade propan-2-ol (Merck). The resulting solution was standardised against freshly sublimed benzoic acid and concentration of the solution was found as 0.047 M. The solution was kept in a refrigerator when not in use as advised in the literature [10,11]. Pyridine, acetonitrile, *N*,*N*-dimethylformamide and acetone were purchased from Merck (99.9 purity) and used without further purification. Ethanol and methanol were purchased from Carlo Erba and dried with Linde type 4A molecular sieve. The azlactone derivatives were synthesized according to the literature [12].

2.2. Apparatus

An Orion Model 720-A digital pH meter with modified combined glass electrode (Ingold) was used for potentiometric titrations. A magnetic stirrer, a semimicro burette with a sensitivity of 0.01 ml was used through this work. All titrations were carried out in beakers of 30 ml volume with temperature control at 25 ± 1 °C.

2.3. Electrode modification and calibration

The combined glass electrode was modified by emptying its internal buffer (aqueous KCl solution) and refilling it with saturated solution of KCl in dry methanol [10]. In order to obtain reliable and reproducible potentiometric titration curves, the potential readings had to be calibrated against a buffer solution with potential readings of −17.0 mV and pH of 7.0 [11]. The modified glass electrode was calibrated and conditioned in the solvents under investigation, and, the upper and lower limits of the potential readings were determined in each solvent against 0.1 M of $HClO_4$ (in dioxane) and 0.1 M of $(C_4H_9)_4$·NOH (in 2-propanol).

Obtained results were in good agreement with literature [13].

3. Results and discussion

3.1. Choice of solvents

Many organic acids [10], and their binary mixtures [11], enols, phenols, imides, Schiff bases [14–19] have successfully been titrated in non-aqueous media. The pH scale in an aqueous solution is governed by K_w (10^{-14}) and the equilibrium in water predicts a potential change of 0.059 V (59 mV) for each unit change in pH for the linear region of equation $E = K + 0.059$ pH [20]. In a similar way, the pH scale in non-aqueous media solvents is governed by the autoprotolysis (autodissociation) constant of the solvent. The chosen solvents having quite small autoprotolysis constants ($K_s = 10^{-n}$ where n is large) were thought to be advantageous for titrations, because their longer millivolt scales provide a better opportunity for precise titrations of the azlactones. The literature [20] quoted autoprotolysis constants/potential ranges of solvents used in this study and the measured values were given in Table 1. Here we used solvents having wide pH scale with a correspondingly longer millivolt range for the potentiometric titrations. The autoprotolysis constant and potential range values of water were also given for comparison.

The suitable acid–base properties of the solvents are also considered. The chosen solvents possessed neutral and basic properties [(*tert*-butanol (neutral/amphiprotic), acetone and acetonitrile (neutral/aprotic), pyridine and dimethylformamide (basic/aprotic)] and the products of titrations were soluble. Dielectric constant, which is a measure of the electrical insulating ability of the solvent, has also an effect on dissociation of oxazolones. In this work, dielectric constants of the chosen solvents were in the range of 12.5–36 Debye and homoconjugation effects were not encountered when the compounds were titrated either in solvent of quite low dielectric constant, pyridine ($\varepsilon = 12.3$ Debye) or in moderate one, acetonitrile ($\varepsilon = 36.0$ Debye).

Table 1
The literature autoprotolysis constants and potential ranges of solvents used in this study [20] and the measured upper and lower potential limits against 0.1 M of $HClO_4$ (in dioxane) and 0.1 M of $(C_4H_9)_4$·NOH (in 2-propanol)

Solvent	K_0	Literature potential range		Measured potential range	
Water	10^{-14}	−300	+240	−317	+222
N,*N*-DMF	$\approx 10^{-18}$	−1000	+270	−900	+237
tert-Butanol	10^{-22}	–	–	−680	−150
Acetonitrile	$10^{-28,6}$	−970	+590	−999	+540
Acetone	$\approx 10^{-30}$	−970	+660	−965	+598
Pyridine	–	−1000	+50	−900	+57

3.2. Potentiometric titration curves of the azlactones

One of the most important targets of this study is to make precise determination of the acidity constants of water-nonsoluble azlactone dyes in non-aqueous media. For this purpose, five analogues of azlactone structures were titrated potentiometrically in the chosen non-aqueous media solvents with a strong quaternary ammonium base (TBAOH).

The computerizable derivative method was used for the end point, and consequently pK_a determination [10]. In the titration of a monoprotic acid with a strong base it is often assumed that, pH = pK_a when $V_b = V_{eq}/2$. At pH = pK_a, $\alpha_{A^-} = 0.5$ so that Eq. (1) can be reduced to Eq. (2).

$$\frac{V_b}{V_a} = \frac{(C_a\alpha_{A^-}) - \Delta}{C_b + \Delta} \quad (1)$$

$$\frac{V_b}{V_a} = \frac{(0.5C_a) - \Delta}{C_b + \Delta} \quad (2)$$

This equation has been applied to calculate the value of V_b/V_a at pH = pK_a where V_a and V_b refer to the initial volumes, C_a and C_b to total analytical concentrations of acid and base, respectively, and Δ is, $\Delta = [H^+] - [OH^-]$.

V_{eq}, is the equivalence point where the added base exactly neutralizes the acid [9]. The titration curves of (between 10^{-3} and 5×10^{-4} M) azlactone derivatives in the solvent of dimethylformamide with 0.047 M quaternary ammonium base (TBAOH) and the related first derivative curves are shown in Fig. 2. Potentiometric titration curves of all azlactone dyes exhibited one well-defined, S-shaped stoichiometric end point. The relative errors were calculated by employing the relative error equation, $Er = [(x_i - x_t)/x_t] \times 100$, where x_i and x_t are the experimental and theoretical equivalence points, respectively (see Fig. 2. Theoretical and experimental equivalence points for **I a**: 1101 μl, and 1114 μl, respectively, relative error values; **I a**: +1.3%, **II a**: +6.6%, **III a**: −4.3%, **IV a**: +1.7%, **V a**: +2.3%). In case of whole titration curves, upper and lower limits of the relative error were between +7.2 and −8.6%.

Using these curves the half neutralization potentials (HNPs) and the related pK_a values were calculated. The half neutralization potentials and pK_a values of the studied azlactone derivatives are listed in Table 2.

The oxazolone derived chromophore units (**I–V**) incorporates four different functional groups namely double bond, carbonyl group, oxygen and nitrogen on the oxazolone ring. The most electropositive center among them is the carbon atom of carbonyl group.

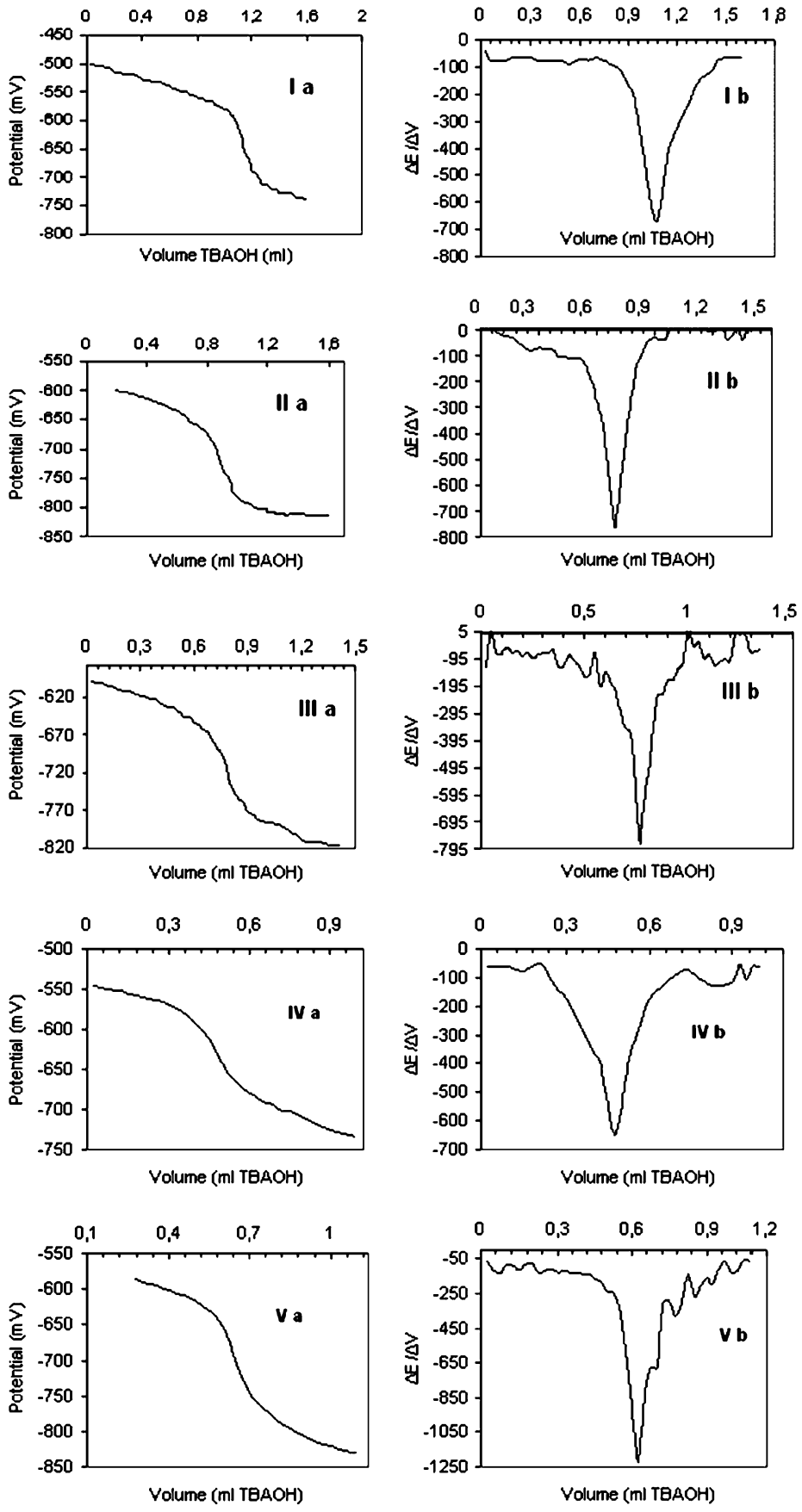

Fig. 2. Potentiometric titration (**I**, **II**, **III**, **IV**, **V-a**) and first derivative (**I**, **II**, **III**, **IV**, **V-b**) curves of five azlactone compounds in the solvent of dimethylformamide with quaternary ammonium base TBAOH.

Table 2
The half neutralization potentials (HNPs) and pK_a values of the studied azlactone dyes

Compound	(HNP; mV) pK_a				
	N,*N*-DMF	*tert*-Butanol	Acetonitrile	Pyridine	Acetone
I	(−532) 11.85	(−501) 11.06	(−587) 11.34	(−540) 12.87	(−250) 15.65
II	(−617) 12.78	(−480) 10.56	(−575) 11.21	(−517) 12.07	(−267) 15.81
III	(−629) 12.88	(−467) 10.34	(−557) 10.81	(−610) 13.89	(−240) 15.57
IV	(−580) 12.56	(−470) 10.39	(−542) 10.44	(−520) 12.09	(−187) 14.09
V	(−598) 12.81	(−490) 10.84	(−548) 10.64	(−530) 12.16	(−248) 15.58

Presence of single-step end points in all titration curves can be attributed to the interaction of TBAOH with carbonyl carbon of oxazolone ring. Otherwise the potentiometric titration curves would contain two or three jumping steps. Irreversible colour changes accompanied the titrations. In the solvent of dimethylformamide, colour of compound **I** changed from "colourless" to "yellow" at the end of the titration. In a similar way, compounds **II**, **III**, **IV** and **V** exhibited colour changes ranging from colourless to dark violet, orange to yellow, yellow to colourless and colourless to yellow, respectively. Observed colour changes can be attributed to the opening of oxazolone ring and the following conjugation change throughout the molecule. Acetone provides the best resolution media for dissociation of oxazolones and excellently differentiates the pK_a values. However, the highest pK_a values were reached in the solvents of *tert*-butanol and pyridine. When the acidities of analogue oxazolone dyes were compared within the same solvent, no remarkable changes in the acidities of the structures were observed. The pK_a values of the oxazolones show that they are nearly neutral or slightly basic in the chosen solvents. However, they are not basic enough to be titrated as bases and they were successfully titrated as acids with TBAOH in all of the chosen solvents.

3.3. Reproducibility studies

The reproducibility of the method was evaluated by successive determinations carried out with three different oxazolone dyes (**III**, **IV** and **V**) in the solvent of acetone under the same conditions as employed for the original determinations. The results are shown in Table 3. As seen from the data in Table 3, the mean HNP values obtained from the reproducibility test are in good agreement with the values shown in Table 2 and the standard deviations (SD) are between mean of HNP ±5.3 and 8.4 mV.

Table 3
The calculated half neutralization potentials (HNPs), the mean values of the five replicate measurements and the standard deviations of the azlactone derivatives **III**, **IV** and **V**

Oxazolone	No. tests	Calculated HNPs (mV) from Table 2	Mean value (mV)	±SD (mV)
III	5	−240	−249	8.4
IV	5	−187	−186	5.3
V	5	−248	−260	6.6

4. Conclusion

Oxazolone derivatives, which are soluble in non-aqueous media, can be titrated potentiometrically with strong quaternary ammonium base of TBAOH with a good precision. The oxazolones exhibit stoichiometric end points corresponding to the interaction of oxazolone ring with TBAOH. Among the five solvents, acetone provides the best resolution medium for the studied oxazolone derivatives. In order to assess the precision of the method, three different azlactone derivatives were tested five times in the solvent of acetone. The averages of the five replicate measurements; standard deviations and agreement of the calculated HNPs with average values were shown. HNP values of oxazolone derivatives can be determined potentiometrically with an average error of less than ±6.7 mV in the employed solvents.

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