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Acridinium Ion Ionization at Elevated Temperatures and Pressures to 200 °C and 2000 bar

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Abstract The temperature and pressure dependences of pK for acridine ion ionization were determined up to 200 °C and 2000 bar. The UV-Vis measurements at high temperatures and pressures were conducted in flow-through spectrophotometric cells. Two independent series of experiment were performed: one in a Ti–Pd cell with silica quartz windows for measurements in the ultraviolet region, and another in a Ti grade 5 cell with sapphire windows for use at higher pressures, which permitted measurements in the visible region. Combined chemometric and thermodynamic analyses of the UV-Vis spectrophotometric data were used to extract the ionization constants as well as the changes in molar volume ΔV° for acridine protonation as functions of temperature and pressure. Values of pK decrease from 5.52 to 3.74 with increasing temperature from 25 to 200 °C at saturated water-vapor pressure. The pressure dependence of acridinium ion ionization is small (e.g., $pK = 5.5$ at 25 °C and 2000 bar) and is characterized by positive $\Delta V^\circ \leq 1.2 \text{ cm}^3 \cdot \text{mol}^{-1}$, which is not surprising for this type of isocoulombic reaction involving a large molecule.

Keywords Acridine · Acridinium ion · Optical pH indicator · Ionization constants · Temperature dependence · Pressure dependence · UV-Vis spectrophotometry

1 Introduction

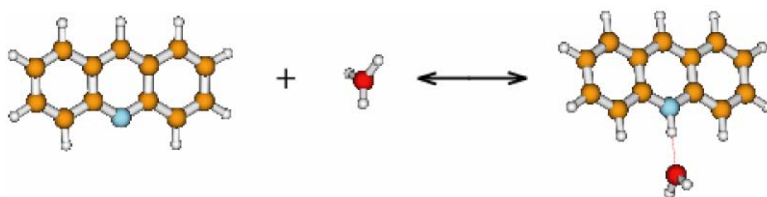
In the fields of corrosion science, chemical processing and synthesis, as well as geochemistry, thermodynamic properties of aqueous solutions under extreme conditions of temperature and pressure are of interest. One such property is pH at hydrothermal conditions. Thermally stable pH indicators have gained some popularity in recent years due to the possibility of being able to measure pH directly in situ when conventional methods, such as potentiometry, have suffered limitations (i.e., limited temperature range for glass electrodes, lower precision for high-temperature ceramic electrodes, etc.). There have been a number of previous studies carried out on the temperature dependence of ionization constants of widely used

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Table 1 Previously reported data for the ionization constant of the acridinium ion at ambient temperature

$t/^\circ\text{C}$	I, M^a	p <i>K</i>	Method	Reference
20	0.01	5.60	UV-Vis spectroscopy	Albert and Goldrace [28]
25	0	5.60	Fluorescence spectroscopy	Rosenberg et al. [12]
25	0	5.42	UV-Vis spectroscopy	Huh et al. [8]
25	0.005	5.54	UV-Vis spectroscopy	Ros et al. [11]
25	0	5.52	Capillary electrophoresis	Jia et al. [13]

^a $M = \text{mol}\cdot\text{dm}^{-3}$

**Fig. 1** Protonation of acridine in acid solutions

indicators such as methyl orange [1, 2], bromphenol blue [3], thymol blue [4], 2-naphthol [5], 2,5-dinitrophenol [6], and *p*- and *o*-nitrophenols [7]. Acridine is of particular interest because of its thermal stability [8–10]. Previous studies have employed different methods (e.g., UV-Vis spectroscopy [8, 10, 11], fluorescence spectroscopy [10, 12], or capillary electrophoresis [13]) to measure the protonation equilibrium of acridine up to 380 °C and 240 bar. There is a difference of up to 0.2 in the reported values of p*K* for acridine ionization (see Table 1), and this difference extends to the values reported at high temperatures by Huh et al. [8] and Ryan et al. [10]. The aim of this study is, therefore, to reexamine the temperature dependence of acridine ionization up to 200 °C at equilibrium saturated vapor pressures, as well as to study the effect of pressure up to 2000 bar.

Acridine is a nitrogen heterocycle structurally related to anthracene, with one of the central carbon atoms replaced by nitrogen (see Fig. 1). In aqueous solutions the acridinium ion and its neutral moiety absorb both in the ultraviolet and visible regions as shown in Figs. 2a and 2b. In acid solutions, the nitrogen atom in the conjugation chain undergoes protonation, resulting in new bands with maxima at 255 and 403 nm.

The UV-Vis spectrophotometric measurements were conducted from 25 to 200 °C and 1 to 2000 bar pressure in order to better characterize the ionization equilibrium of acridinium ion as given by,



2 Experimental Part

All solutions were prepared using Nanopure Millipore (resistivity $\geq 18 \text{ M}\Omega\cdot\text{cm}^{-1}$) deionized water. The water was degassed under partial vacuum in an ultrasonic bath, and periodically purged with oxygen-free argon that was obtained by passing argon (grade 4.8) through a column of copper filings at 425 °C.

An acetic acid stock solution ($0.199 \text{ mol}\cdot\text{kg}^{-1}$) was prepared by mass from glacial acetic acid (Merck, extra pure). A sodium acetate stock solution ($0.211 \text{ mol}\cdot\text{kg}^{-1}$) was prepared by dissolving the anhydrous sodium salt in water (Fluka, $\geq 99.5\%$). Perchloric and hydrochloric acids were diluted from the concentrated acids (HClO_4 , 60%, p.a., Merck; HCl , 30%, suprapur, Merck) and standardized by colorimetric and potentiometric titration against Trisma-base (Tris(hydroxymethyl)aminomethane, 99+%, Aldrich) using methyl red as the indicator. A sodium hydroxide solution ($0.082 \text{ mol}\cdot\text{kg}^{-1}$) was prepared by dilution of a saturated sodium hydroxide solution (50% solution in water, Aldrich) with CO_2 -free water, and standardized under argon pressure (slightly above atmospheric) by potentiometric and colorimetric titration against standardized the perchloric acid using methyl red as an indicator. The prepared solution was stored in a flask connected with a glass tube filled with ascarite (Fluka, 5–20 mesh) and drierite (Fluka, + 4 mesh) in order to keep it CO_2 -free. The pH of the studied solutions was controlled by various combinations of the above-mentioned reagents. The pH was measured at atmospheric pressure and room temperature with a glass combination electrode (Metrohm), calibrated every day against at least two standard buffer solutions.

Acridine (Aldrich, 97%) was purified by recrystallization from ethanol and dried at 100°C until constant weight was attained. Because of its very low solubility in pure water, stock solutions of acridine were prepared in dilute acid. The acridine solutions were prepared with degassed (deoxygenated) water as mentioned above in order to avoid oxidation, especially at elevated temperatures [9]. The prepared stock solutions of acridine were stored under argon and protected from light. Freshly diluted solutions were made prior to each experiment, and then degassed and purged with deoxygenated argon just before the measurements were made.

Initially, we decided to study the spectra of acridine in perchloric acid solutions. A stock solution of acridine ($2.2 \text{ mmol}\cdot\text{kg}^{-1}$) was prepared in $0.063 \text{ mol}\cdot\text{kg}^{-1}$ perchloric acid. However, after one week of storage the solution had changed in color from lemon yellow to dark yellow, and long acicular orange crystals began to precipitate. In addition, the spectrum of acridine dissolved in the perchloric acid was observed to change over a period of 30 minutes at 25°C . The presumed oxidation of acridine by perchloric acid therefore precluded the use of the latter solute to define and adjust the pH in our experiments. More dilute (~ 0.3 to $0.5 \text{ mmol}\cdot\text{kg}^{-1}$) acridine stock solutions prepared with acetic acid appeared to be stable, and no precipitates were observed in solutions stored for up to a month. Spectra of solutions in which the pH was adjusted with hydrochloric and acetic acid, or acetate and sodium hydroxide, showed no change over 30 min at any studied temperature and pressure, which is consistent with the observation of Ryan et al. [10] and in contrast to the observation of Bulemela et al. [14] who reported that absorbance of acridine decreased by 0.9 % per minute at both at 25 and 250°C . These differences might be caused by oxidation processes in non-deoxygenated aqueous acridine solutions, as suggested was by Lee et al. [8, 9].

Two independent series of experiments were conducted in order to determine the temperature and pressure dependences of acridinium ion ionization.

2.1 Case 1. Temperature Dependence

These experiments were aimed at determining the variation of the equilibrium constant, K , for the deprotonation of the acridinium ion as a function of temperature at water saturated vapor pressure. A high-temperature, flow-through spectrophotometric system [15, 16] was used to conduct experiments at six temperatures from 25 to 200°C . The optical cell was made of titanium-palladium alloy provided with cylindrical (5 mm thick) silica glass windows in a screwed-cap design. The solutions were pumped into the cell with a HPLC pump

(PrepStar, Varian) and purged of dissolved gases with an on-line vacuum degassing system (Alltech). All of the connection parts that were in contact with the solution were made of PEEK[®] (including the head unit in the HPLC pump) or Teflon[®]. The pressure was monitored with the pressure module inside the HPLC pump and controlled by a back-pressure regulator (Upchurch Scientific High Pressure Adjustable BPR), and maintained at 10 bar above the saturation water vapor pressure at each temperature. The spectra were collected with a Varian Cary 5 double-beam spectrophotometer in the 190 to 500 nm wavelength range at 0.5 nm intervals, with a 60 nm·min⁻¹ scanning rate. Three consecutive spectra were taken for each solution at each temperature and pressure. The cell was flushed with fresh solution at each studied temperature to avoid the presence of any possible decomposition products of acridine that might form with time at elevated temperatures. To allow for thermal equilibration, spectra were measured 15 min after the desired temperature was reached. For the data treatment, the ultraviolet part of the spectrum at 240 to 260 nm was used where the neutral and protonated forms have intense, well-separated peaks (Fig. 2a). The total concentration of acridine was low and ranged from 3.4 to 4.7 μmol·kg⁻¹.

2.2 Case 2. Pressure Dependence

The second series of experiments was conducted in order to study the dependence of acridinium ion deprotonation reaction on pressure. The UV-Vis spectrophotometric measurements were carried out from 25 to 150 °C and from 100 to 2000 bar, using a Cary 4000 spectrophotometer and a flow-through spectrophotometric cell [17]. The cell was made from titanium grade 5 alloy and equipped with sapphire windows sealed with elastomeric graphite (GraFlex) using a Bridgeman-type seal, and was connected to the spectrophotometer with fiber-optic cables. Pressure was generated with a 7 cm³ titanium grade 5 spindle press, automatically controlled by a powerful stepping motor using a custom made PID (proportional-integral-derivative) controller. The pressure was measured with a strain gauge pressure transducer calibrated against a Heise[®] Bourdon tube pressure gauge. Before each measurement (i.e., at each studied temperature), the cell was flushed with fresh solution. The visible part of the spectra (320 to 450 nm) was used for the data treatment (Fig. 2b). Because the absorbance in this region is less intense than in the ultraviolet region, the solutions analyzed in the cell with sapphire windows were five to ten times more concentrated (i.e., in the range from 2.5 to 8.3 μmol·kg⁻¹) than those studied at equilibrium saturated vapor pressures (case 1).

3 Data Treatment

The collected spectra were stored in an absorbance matrix, $A_{i \times j}$, where i = number of wavelengths and j = number of analyzed solutions. Water, sodium hydroxide, acetic acid and sodium acetate baseline spectra were measured separately at each of the temperatures studied. The acridine spectra were corrected for background absorbance (i.e., windows plus solvent). In order to determine the number of absorbing species (rank or number of principal components) required for a chemical model, we used the singular value decomposition (SVD) method:

$$A_{i \times j} = U_{i \times n} \times S_{n \times n} \times V_{j \times n}^T, \quad (2)$$

where the matrixes U , S , V are the result of singular value decomposition of the matrix A , U is the $i \times n$ matrix of the left singular vectors that form an orthonormal basis for

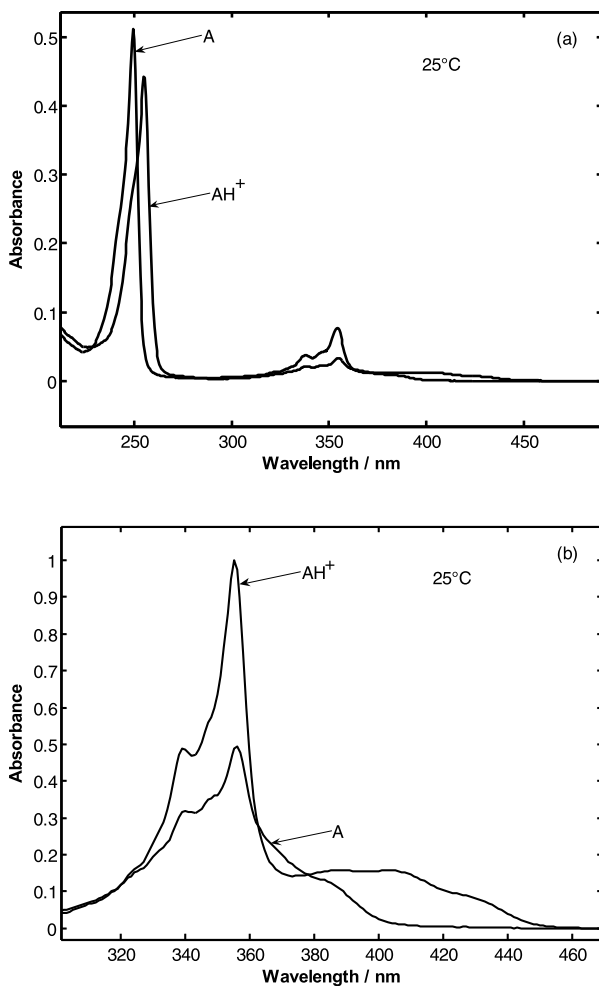


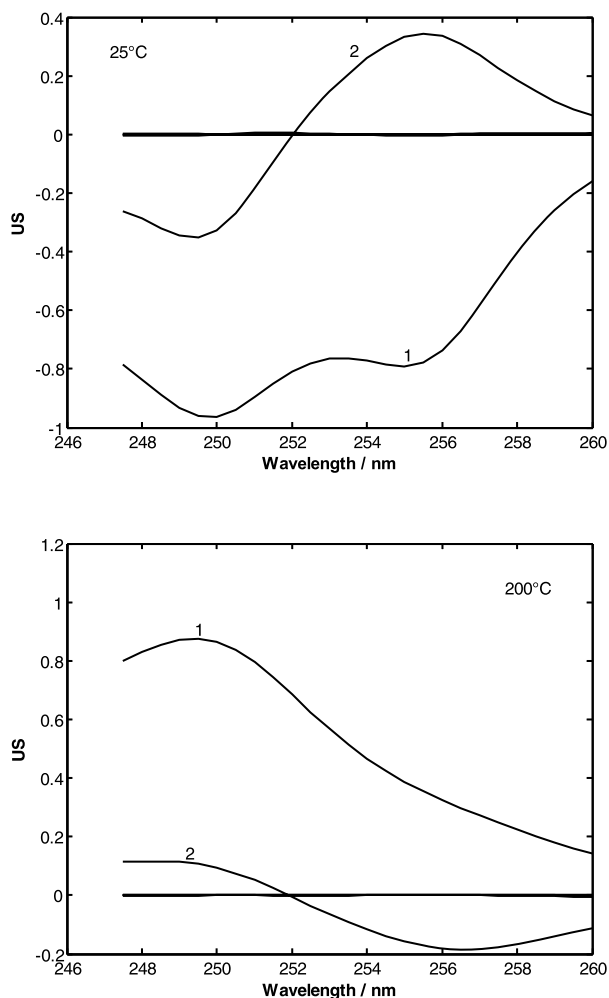
Fig. 2 Spectra of acridine and the acridinium ion at 25 °C corrected for background absorbance: **(a)** over the whole range of studied wavelengths, $[A] = 3.27 \times 10^{-6} \text{ mol}\cdot\text{kg}^{-1}$ and $[AH^+] = 3.96 \times 10^{-6} \text{ mol}\cdot\text{kg}^{-1}$; **(b)** details of the fine structure of the absorption spectrum in the visible region, $[A] = 5.1 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$ and $[AH^+] = 5.17 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1}$

the absorption profile, \mathbf{S} is the $n \times n$ diagonal matrix of singular values, and \mathbf{V} is the $n \times j$ matrix of right singular values that form an orthonormal basis for the concentration-dependence response. By convention, the ordering of the singular vectors is determined by high-to-low sorting of the singular values, with the highest singular value being the upper left index of the matrix. One important result of the singular value decomposition of \mathbf{A} is that

$$\mathbf{A}^{(l)} = \sum_k \mathbf{U}_k \times \mathbf{S}_k \times \mathbf{V}_k^T \quad (3)$$

is the rank- l matrix closest to our original absorbance matrix $\mathbf{A}_{i \times j}$, (i.e., $\mathbf{A}^{(l)}$ minimizes the sum of the squares of the difference of the elements of \mathbf{A} and $\mathbf{A}^{(l)}$). In Fig. 3 one

Fig. 3 The contribution of the most significant vectors to the total absorbance at 25 and 200 °C, where matrices U and S are the results of SVD of the absorbance matrix



can see the product of U and S matrices plotted against the wavelength, indicating the contribution of the most significant vectors to the absorption profile. Such a procedure was repeated at each studied temperature, and demonstrated that only two vectors are needed to represent more than 99% of the raw absorption data, and all the other vectors are randomly oscillating around zero and therefore were discarded as most probably corresponding to random instrumental noise and small uncertainties in the solution preparation.

After the number of absorbing species has been determined, the chemical model can be described as a system of eight linear equations which are now given.

The equilibrium constant for acridinium ion ionization (see Eq. 1) is given by:

$$K = \frac{[A]\gamma_A[H^+]\gamma_{H^+}}{[AH^+]\gamma_{AH^+}}, \quad (4)$$

where K is an ionization constant, A denotes the neutral acridine species, and AH^+ denotes the protonated form (i.e., the acridinium ion). The charge-balance equation is:

$$[CH_3COO^-] + [OH^-] + [Cl^-] = [H^+] + [Na^+] + [AH^+] \quad (5)$$

and the three mass-balance equations for total Na, acetate and acridine are, respectively,

$$[Na_{tot}] = [CH_3COONa + Na^+], \quad (6)$$

$$[CH_3COO_{tot}] = [CH_3COOH] + [CH_3COONa] + [CH_3COO^-], \quad (7)$$

$$[A_{tot}] = [AH^+] + [A]. \quad (8)$$

For the ionization of water, sodium acetate and acetic acid, respectively,

$$K_w = [H^+]\gamma_{H^+}[OH^-]\gamma_{OH^-}, \quad (9)$$

$$K_{acetate} = \frac{[CH_3COO^-]\gamma_{CH_3COO^-}[Na^+]\gamma_{Na^+}}{[CH_3COONa]\gamma_{CH_3COONa}}, \quad (10)$$

$$K_{acetic} = \frac{[CH_3COO^-]\gamma_{CH_3COO^-}[H^+]\gamma_{H^+}}{[CH_3COOH]\gamma_{CH_3COOH}}. \quad (11)$$

The terms in square brackets are the molal concentrations of the indicated species, and γ is the molal activity coefficient of the corresponding species that is taken as unity for uncharged species (e.g., γ_{CH_3COONa} , γ_{CH_3COOH} and γ_A). Activity coefficients for charged species were calculated using a Debye-Hückel equation:

$$\log_{10} \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + Ba_i^0\sqrt{I}}, \quad (12)$$

where the Debye-Hückel limiting-slope parameters A and ion-size parameter B , as a function of temperature and pressure, were taken from Ref. [18]. The maximum ionic strength in all solutions was always $\leq 0.02 \text{ mol}\cdot\text{kg}^{-1}$ and generally $< 0.001 \text{ mol}\cdot\text{kg}^{-1}$. The iterative calculation procedure was based on successive approximations, with the initial assumption that all the activity coefficients were equal to unity.

The calculations were carried out on the molal scale and conversion to the molar units of Beer's law was facilitated by using temperature-dependent density data for water (given the low concentration of acridine). The densities of pure water at different temperatures and pressures were taken from Hill [19]. The relevant values for the ion product constant of water, K_w , as a function of temperature and pressure were taken from Marshall and Franck [20]. The ion-pair constants for sodium acetate and sodium hydroxide association were taken from Shock and Koretsky [21] and Ho and Palmer [22], respectively. However, for the dilute solutions and temperatures and pressures studied, the formation of sodium acetate and hydroxide ion pairs is negligible. Their inclusion in the computational scheme contributed only to the third decimal place for pK of acridine at 200°C (less at the higher pressures), which is much smaller than the experimental error. The values of pK for acetic acid up to 200°C at saturated vapor pressure were taken from the precise conductivity data of Ellis [23], which are identical to the "smoothed" literature compilation given by Mesmer

et al. [24]. The pressure dependence of the ionization constant of acetic acid was taken from the conductivity study of Lown et al. [25], which gives values of the equilibrium constant up to 225 °C and 3000 bar.

The pK of acridinium ion deprotonation was obtained using following equation:

$$l \times \epsilon \times C = A = U_{i \times n} \times S_{n \times n} \times V_{j \times n}^T, \quad (13)$$

where the left part of this equation represents Beer's law in which the scalar term, l , is the optical path length, ϵ is the $i \times n$ matrix of molar absorptivities and C is the $n \times j$ matrix of the molar concentrations of absorbing species. Matrix C is obtained from the solution of the system of eight linear equations describing the chosen chemical model (see above). The change in optical path length with temperature up to 350 °C is negligible [16]. The right-hand-side of the Eq. 13 is the SVD of the absorbance matrix, A , with n absorbing species ($n = 2$). The calculation procedure involving matrix manipulations using Matlab 7.0 and Maple 8 computational platforms, and is described in detail elsewhere [26].

4 Results and Discussion

The spectra of neutral acridine and its protonated form over the whole range of studied wavelengths at 25 °C are shown in Fig. 2. In the UV region from 200 to 270 nm, the absorbance maximum for acridinium ion occurs at 255 nm and for acridine at 249.5 nm, while still in visible region, the absorbance intensity is much smaller with the maxima occurring at 355 and 356 nm for the acridinium ion and acridine, respectively, with an additional peak for acridinium ion occurring at 403 nm.

4.1 Temperature Dependence

The spectra of acridine at different pHs are shown in Fig. 4. At pH = 3.86, the spectrum is due predominantly to the HA^+ species. With increasing pH, the formation of deprotonated (neutral) acridine (A) proceeds such that at pH = 9.95 the spectrum is due solely to the neutral species.

Fig. 4 Absorbance of aqueous acridine solutions at 25 °C as a function of pH for $[Acr_{tot}]$ concentrations ranging from 3.4×10^{-6} to $4.6 \times 10^{-6} \text{ mol} \cdot \text{kg}^{-1}$

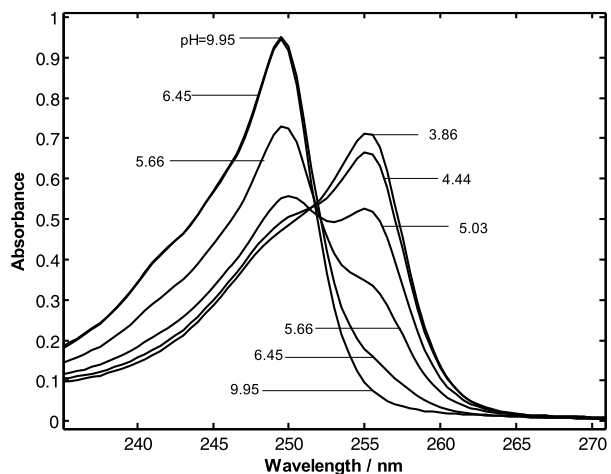


Table 2 Temperature dependence of the ionization constant of acridinium ion with their two sigma confidence interval calculated by a Monte Carlo method given in parentheses (see the text for details)

$t/^\circ\text{C}$	$\log_{10} K (\pm 2\sigma)$
25	-5.52 (± 0.02)
50	-5.15 (± 0.02)
75	-4.85 (± 0.02)
100	-4.56 (± 0.03)
150	-4.17 (± 0.04)
200	-3.74 (± 0.04)

The absorbance maximum of neutral acridine occurs in the ultraviolet region and stays at 249.5 nm with increasing temperature up to 150 °C (Fig. 5a). At 200 °C, the band maximum undergoes a weak blue shift to 249.0 nm, whereas for the acridinium ion the absorbance maximum undergoes a weak red shift from 255.0 to 256.0 nm (Fig. 5b) between 25 and 200 °C. The spectra of both species (A and AH⁺) in the visible region undergo a small red shift with increasing temperature to 200 °C (i.e., it changes from 355.0 to 356.0 nm for species A and from 354 to 355.5 nm for AH⁺). Increasing the temperature causes significant changes in the absorption spectrum of a solution that initially contained more than 98% of fully protonated acridine at 25 °C and pH_{25°C} = 3.86 (Fig. 5c); this is a result of increasing ionization of the acridinium ion (Fig. 5c). The molar absorptivities of both species at 25 and 200 °C are shown in Fig. 6.

Values of ionization constants for the acridinium ion at different temperatures are shown in Table 2 and are plotted, together with available literature data, in Fig. 7. The uncertainties in pK were evaluated using a Monte Carlo simulation of experimental errors arising from the solution preparations, temperature and absorbance. The influence of temperature uncertainty on the density of water and ionization constants of acetic acid, sodium acetate and water, as well as solution preparation, were evaluated separately with the same principle using 10⁴ iterations based on a Monte Carlo method. Our pK values at 25 and 50 °C are in perfect agreement with those reported by Ros et al. [11] and Jia et al. [13], whereas the high-temperature data of Huh et al. [8] and Ryan et al. [10] (both derived by UV-Vis methods) are lower by about 0.1 and 0.2 log units, respectively, at each studied temperature. This difference is larger than the indicated confidence interval. The reason for this difference is not clear.

Since the ionization reaction for the acridinium ion is isocoulombic (Eq. 1), the dependence of log₁₀ K on 1/T is expected to be close to linear (Fig. 8). The linearity of this plot also indicates both that ΔC_p ≈ 0 for the reaction and that the dependence of log₁₀ K versus T can be described with the classic van't Hoff equation:

$$\log_{10} K = a + \frac{b}{T}, \quad (14)$$

where $a = -0.78794$ and $b = -1411.767$.

Equation 14 was differentiated with respect to the temperature in order to obtain the enthalpy (ΔH°) and entropy (ΔS°) for the deprotonation of acridine:

$$\Delta H^\circ = \left(\frac{\partial(\Delta G^\circ/T)}{\partial(1/T)} \right)_p = RT^2 \frac{\partial \ln K}{dT} \quad (15)$$

and

$$\Delta S^\circ = - \left(\frac{\partial \Delta G^\circ}{\partial T} \right)_p. \quad (16)$$

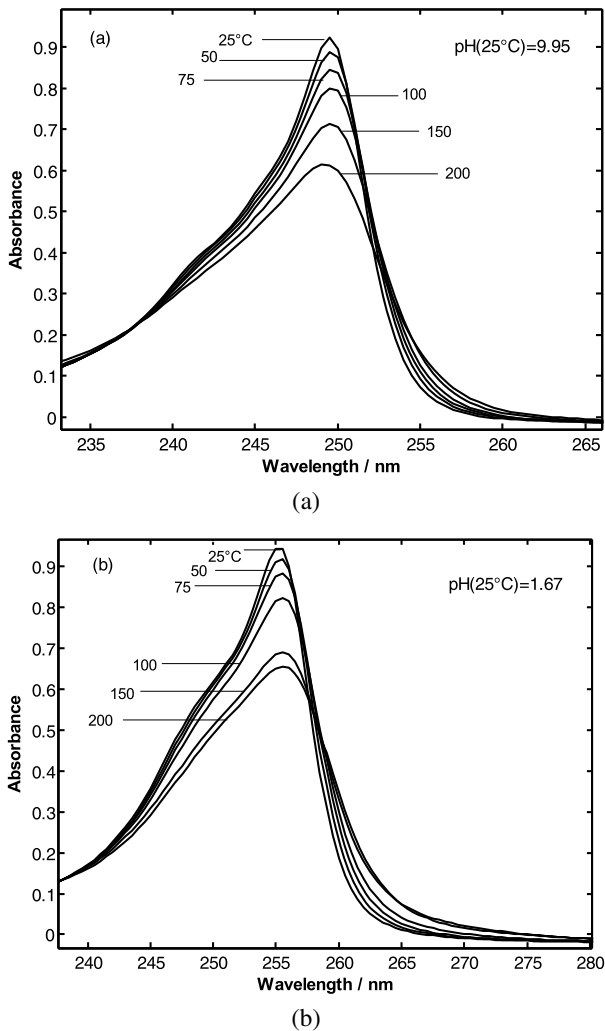


Fig. 5 Spectra of aqueous acridine solutions at different temperatures: **(a)** pH = 9.95, [Acr_{tot}] = 3.38 × 10⁻⁶ mol·kg⁻¹; **(b)** pH = 1.67, [Acr_{tot}] = 4.77 × 10⁻⁶ mol·kg⁻¹; **(c)** pH = 3.86, [Acr_{tot}] = 3.44 × 10⁻⁶ mol·kg⁻¹

Over the temperature range up to 200 °C and at equilibrium saturated vapor pressure, the ionization reaction of acridine is characterized by an endothermic enthalpy ($\Delta H^\circ = +27.01 \text{ kJ}\cdot\text{mol}^{-1}$) and small negative entropy ($\Delta S^\circ = -15.08 \text{ J}\cdot\text{mol}\cdot\text{K}^{-1}$).

4.2 Pressure Dependence

Figure 9 shows the measured spectra of acridine-containing solutions at different pressures at 50 °C. The absorbance increase is mainly due to the higher molar concentration of acridine with increasing pressure, because of the volume decrease resulting from compressing the solution. No shift in band position with increasing pressure was detected, either in basic or acidic solutions.

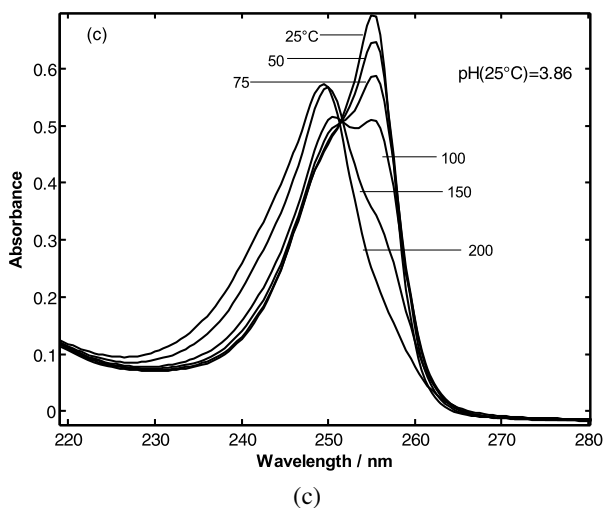


Fig. 5 (Continued)

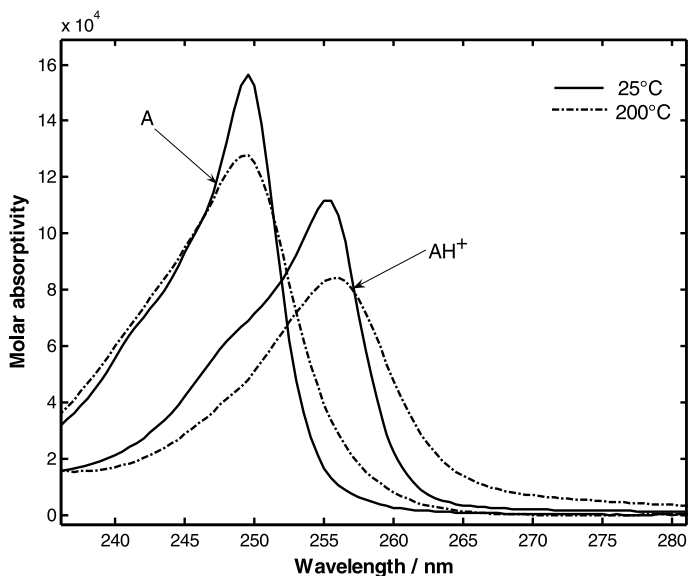


Fig. 6 Molar absorptivities of acridine and the acridinium ion at 25 and 200 °C

The effect of pressure changes on the acridinium ion ionization constant with increasing temperature is given to 150 °C in Table 3 and shown in Fig. 10. The pressure dependence of the acridinium ion ionization constant is very small over the studied temperature interval. The change in partial molar volume for the ionization reaction, ΔV° , and partial molar compressibility change, $\Delta\kappa^\circ$, can be evaluated with the following equations:

$$\Delta V^\circ = \left(\frac{\partial G^\circ}{\partial p} \right)_T = - \left(\frac{\partial RT \ln K}{\partial p} \right)_T, \tag{17}$$

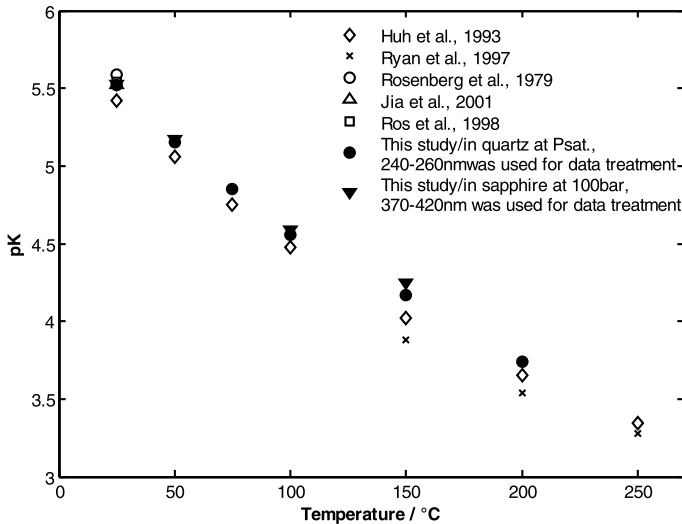


Fig. 7 Temperature dependence of the ionization constant of the acridinium ion compared with available literature data

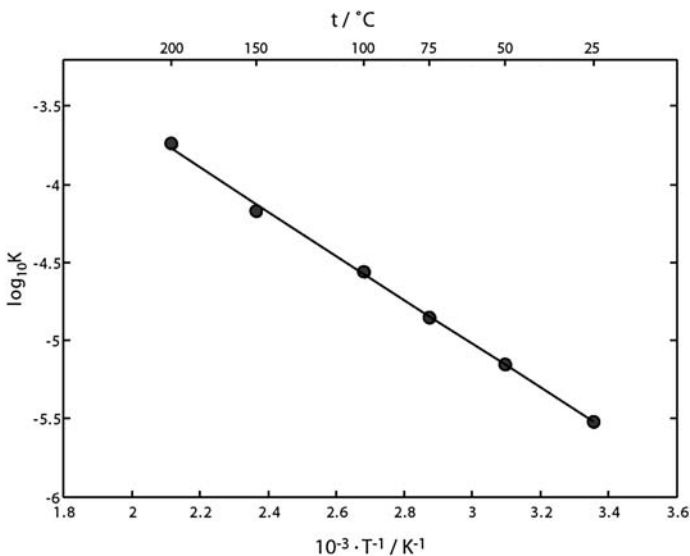


Fig. 8 Van't Hoff plot for the ionization constant of the acridinium ion (experimental values obtained at saturated vapor pressure, and a linear fit with the R^2 value)

$$\left(\frac{\partial \Delta V^\circ}{\partial p} \right)_T = -\Delta k^\circ. \quad (18)$$

Because the values of pK are constant at each temperature over the studied pressure interval (all changes in pK with pressure are within experimental error), ΔV° is considered to be constant with a value of $0.0 \pm 1.2 \text{ cm}^3 \cdot \text{mol}^{-1}$. It follows that the partial molar

Fig. 9 Spectra of acidic and alkaline solutions of acridine at 50 °C as a function of pressure

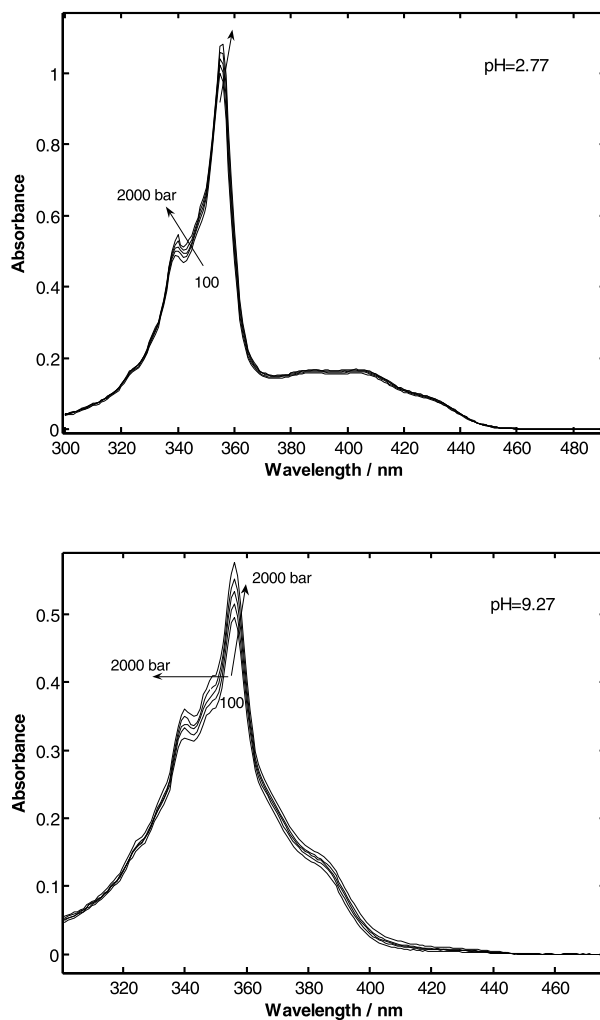


Table 3 The experimentally derived values of pK for the ionization of the acridinium ion as a function of temperature and pressure

$t/^\circ\text{C}$	$\log_{10} K$					$\pm 2\sigma$
	100 bar	500 bar	1000 bar	1500 bar	2000 bar	
25	-5.53	-5.54	-5.55	-5.55	-5.55	0.02
50	-5.17	-5.17	-5.18	-5.17	-5.17	0.02
100	-4.59	-4.59	-4.58	-4.58	-4.57	0.04
150	-4.25	-4.25	-4.24	-4.23	-4.20	0.04

compressibility is therefore zero. Such a small pressure effect is also found for imidazol, another heterocyclic compound whose pK is “insensitive” to increasing pressure up to 6000 bar [27].

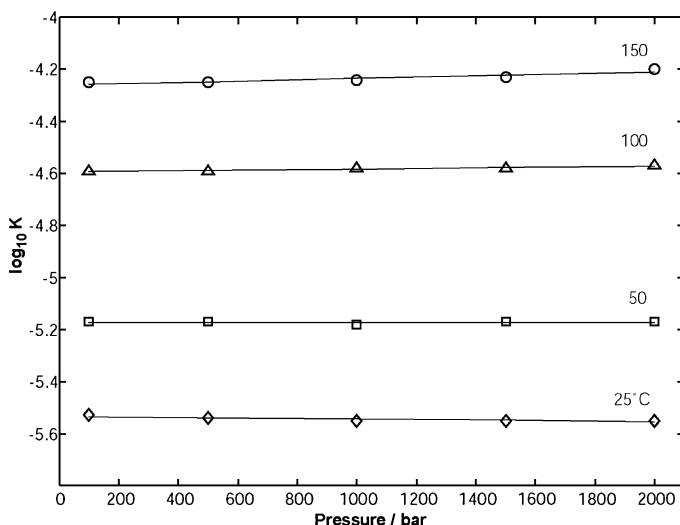


Fig. 10 Pressure and temperature dependence of the ionization constant for the acridinium ion

Because the pressure dependence was studied from 25 to 150 °C, we can also retrieve the temperature dependence of the ionization constant for the acridinium ion. The lowest studied pressure was 100 bar, but because the pressure effect is very small, we can compare this value directly with our values obtained at saturated vapor pressure. Therefore, we have two “independent” sets of constants (different sets of the solutions were used and the total concentration of acridine differed by one order of magnitude). The spectra of solutions were measured in different cells using different spectrophotometers. In addition, different spectral regions were used in the derivation of the two sets of acridine *pK* values (i.e., UV spectra for the saturated vapor pressure values given in the Table 2, and the visible spectra for the higher pressure data given in Table 3). The two sets of data at saturated vapor pressure of water and at 100 bar are in good agreement.

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