

UV–visible spectrum of nitrous acid in solution: pK_a determination and analytical applications

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Abstract

The UV–visible spectra of nitrous acid in four different solvents were obtained. The hyperfine structure observed in all these spectra was tentatively attributed to vibrational coupling. The unique characteristics of the nitrous acid spectrum in acidic solution allowed the detection and determination of 3.0×10^{-4} mol l^{-1} nitrite in the presence of 0.1 mol l^{-1} nitrate solution. Through spectrophotometric and potentiometric measurements, the pK_a value for nitrous acid was calculated to be 2.3 ± 0.2 .

Keywords: UV–Visible spectrophotometry; Dissociation constants; Nitrate; Nitrite; Nitrous acid

The simultaneous analytical determination of nitrate and nitrite has been performed by many methods [1–4]. One of these methods [4] does not involve the addition of any reagent to the sample, and takes advantage of the fact that aqueous $NaNO_2$ exhibits an absorption band at 355 nm whereas aqueous $NaNO_3$ shows no absorption at this wavelength. Wetters and Uglum [4] also mentioned that at $pH < 5.0$, the spectrum of nitrous acid begins to appear in $NaNO_2$ aqueous solutions. Although recognizing the unique characteristics of the nitrous acid spectrum, they did not consider this aspect further.

In this work, the UV–visible spectra of nitrous acid in aqueous solutions and in other solvents were obtained and a specific method for NO_2^-

detection was developed. The dissociation constant of nitrous acid was redetermined by two independent methods.

EXPERIMENTAL

Apparatus

Spectrophotometric measurements were made with a Hewlett-Packard HP 8452A diode-array spectrophotometer and a Hitachi U-3210 spectrophotometer utilizing 1-cm quartz cells.

All pH measurements were made on a Corning Model 130 pH meter equipped with a Corning Model 476541 semi-micro electrode.

Reagents

All the reagents used (Merck and Aldrich) were of analytical-reagent grade. Nitrite and nitrate solutions were standardized spectrophotometrically by Wetters and Uglum's method [4].

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The solvents employed (Merck) were purified according to the literature [5] just before use. Doubly distilled water was used throughout.

Procedure

The UV–visible spectra of nitrous acid solutions were obtained in $\text{CF}_3\text{COOH}-\text{CF}_3\text{COONa}$ solutions in the pH range 0.24–4.00. For $\text{p}K_a$ calculations, all the measurements were made 5 min after the addition of sodium nitrite solution to $\text{CF}_3\text{COOH}-\text{CF}_3\text{COONa}$ solution. CF_3COONa was used as a background electrolyte for maintaining the ionic strength constant.

An uncertainty of ca. ± 1.0 nm (ca. 66 cm^{-1}) could be assigned to the attribution of λ_{max} in the spectra.

From absorbance measurements at 347, 358, 372 and 386 nm it was possible to calculate the dissociation constant of nitrous acid (HONO) by using the equation [6]

$$\text{p}K = \text{pH} + \log \left(\frac{A_o - A_{\text{NO}_2^-}}{A_{\text{HONO}} - A_o} \right)$$

where A_o is the absorbance at the chosen wavelength for the mixture of the two forms at a particular pH and $A_{\text{NO}_2^-}$ and A_{HONO} are the absorbance of the basic and acidic forms, respectively.

The $\text{p}K_a$ for HONO was also calculated from pH measurements on HONO– NaNO_2 aqueous solutions. In these experiments the ionic strength was maintained at 1.0.

The pH meter was calibrated using 1.00×10^{-3} mol l^{-1} CF_3COOH solutions in CF_3COONa

medium ($\mu = 0.10-1.00$). Therefore, the pH measurements are referred to hydrogen ion concentration and not activity.

RESULTS AND DISCUSSION

In aqueous solutions HONO exhibits four distinct absorption peaks at 386, 372, 358 and 347 nm. In addition to these peaks, two shoulders can be easily observed at 337 and 325 nm (see Table 1 and Fig. 1).

Similarly to the absorptions observed in the UV–visible spectra of NaNO_2 solutions [4], the above absorptions for HONO solutions are of low intensity and probably originate from forbidden transitions of the nitrous acid molecule. The hyperfine structure of the HONO spectrum is probably a consequence of a vibrational coupling [7].

This hyperfine structure is also present in the UV–visible spectra of HONO in methanol, acetonitrile and benzene (Fig. 1). In addition to the six peaks mentioned above, a seventh absorption process is observed in methanol and in water.

The molar absorptivities of the transitions increase as the polarity of the solvent decreases. Also, the energy of the transition increases as the polarity of the solvent decreases. The major shift in energy observed in the HONO spectra on changing from water to benzene medium corresponds to only to 0.8 kcal (1 kcal = 4.184 kJ) (337–334 nm).

The average energy difference between the peaks present in the hyperfine structure in Fig. 1

TABLE 1
Molar absorptivities of HONO in different solvents

Solvents	Parameter	Values						
Water	$\lambda(\text{nm})$	386	372	358	347	337	325	318
	$\epsilon(\text{l mol}^{-1} \text{cm}^{-1})$	31.3	52.0	51.2	38.6	25.0	~ 15	~ 11
Methanol	$\lambda(\text{nm})$	386	366	353	341	330	320	312
	$\epsilon(\text{l mol}^{-1} \text{cm}^{-1})$	15.0	54.8	81.4	77.7	58.8	37.3	24.9
Acetonitrile	$\lambda(\text{nm})$	388	373	360	348	337	327	^a
	$\epsilon(\text{l mol}^{-1} \text{cm}^{-1})$	36.6	61.3	58.0	38.5	23.1	13.2	–
Benzene	$\lambda(\text{nm})$	387	371	357	345	334	323	^a
	$\epsilon(\text{l mol}^{-1} \text{cm}^{-1})$	91.4	257.1	372.0	356.3	374.4	179.8	–

^a It is difficult to observe this band in these solvents owing to their strong absorption in this region.

is about 1.0×10^3 and $9.3 \times 10^2 \text{ cm}^{-1}$ for benzene and water as solvent, respectively. Benzene is not a polar solvent, hence little influence of the solvent on the characteristics of the spectra [8] is expected and the UV–visible spectra of HONO in benzene and in the gaseous phase are expected to be similar.

In the gaseous phase the HONO molecule exhibits *cis* and *trans* configurations that are easily interconvertible as the difference in energy between the forms is only about $0.51 \text{ kcal mol}^{-1}$ [9]. Both the *cis* and *trans* forms of nitrous acid absorb near 850 cm^{-1} due to the N–O stretch ν_4 [9,10]. The nitrite ion does not exhibit absorption bands in this region.

Taking into account the experimental uncertainties in the attribution of λ_{max} in the UV–visible spectra and in the NO_2^- and HONO vibra-

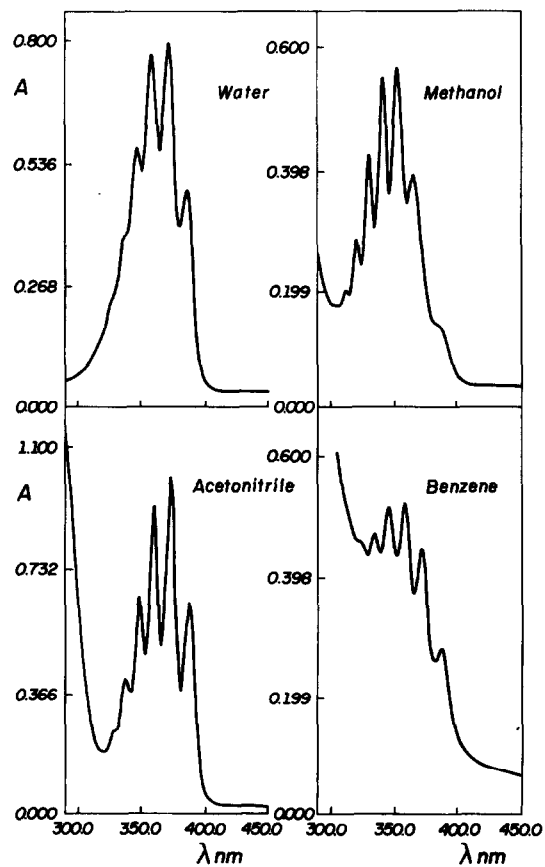


Fig. 1. UV–visible spectra of HONO in different solvents.

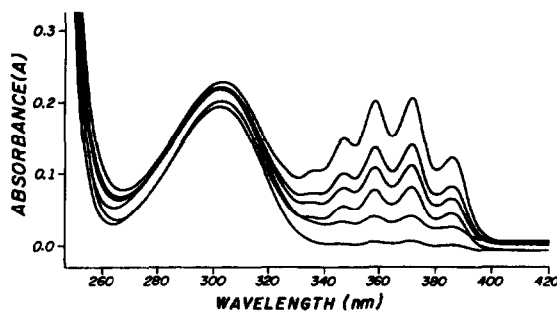


Fig. 2. UV–visible spectra of nitrite and nitrate mixtures at pH 1.0. Concentrations: $\text{NaNO}_3 = 0.03 \text{ mol l}^{-1}$; $\text{NaNO}_2 = 3.0 \times 10^{-4}$, 7.5×10^{-4} , 1.5×10^{-3} , 2.3×10^{-3} and $4.5 \times 10^{-3} \text{ mol l}^{-1}$.

tional spectra [4,10], it is reasonable to ascribe the hyperfine structure to the coupling of the electronic transition with the vibrational component ν_4 [9]. The value of 850 cm^{-1} corresponds to the energy gap between two vibrational levels at the ground state and as in the vibronic–electronic coupling the differences are between the vibrational levels of the excited states, 850 cm^{-1} should be considered only as a reference value.

Owing to the unique characteristics of the UV–visible spectra of HONO acidic solutions, it provides a selective and useful method for detecting nitrite contamination in samples. It is possible to identify and determine NaNO_2 at concentrations down to $3.0 \times 10^{-4} \text{ mol l}^{-1}$ in 0.1 mol l^{-1} NaNO_3 solution (see Fig. 2), provided that the hydrogen ion concentration is properly adjusted with CF_3COOH . This limit would be decreased by one order of magnitude if a 10-cm path-length cell were to be employed. The NO_2^- detection can be performed without interference in the presence of $1.0 \times 10^{-1} \text{ mol l}^{-1}$ of the following ions: ClO_4^- , CF_3SO_3^- , Cl^- , BF_4^- , Br^- , CH_3COO^- , SO_4^{2-} , PO_4^{3-} and PF_6^- .

This procedure has proved useful in detecting NaNO_2 impurities in isolated nitrosyl ruthenium complexes of the type *trans*- $[\text{Ru}(\text{NH}_3)_4\text{LNO}]$ - $(\text{PF}_6)_3$ (see Fig. 3).

The absorbance of aqueous HONO solution changes with time. A decrease in absorbance is observed for the peaks corresponding to the nitrous acid. For $\lambda_{\text{max}} = 372 \text{ nm}$, the molar absorptivity is 52.0, 49.9, 48.0, 46.8 and $46.0 \text{ l mol}^{-1} \text{ cm}^{-1}$

after 5, 10, 15, 20 and 25 min, respectively. In spite of the absorbance changes, very good straight lines were obtained for plots of absorbance versus NO_2^- concentration when the data were referred to the same measured time. For all the plots, the correlation coefficient was never worse than 0.990. For instance, for absorbance measurements at 372 nm carried out 5 min after acidification of nitrite solution, the correlation coefficient was 0.999; the slope and the standard deviation of the slope were 52.0 and 2.22 ($n = 6$), respectively, and the intercept and the standard deviation of the intercept were 8.20×10^{-4} and 7.70×10^{-3} ($n = 6$), respectively. Therefore, this spectrophotometric method can be also used for quantitative purposes.

The $\text{p}K_a$ of HONO is another point that deserves comment. Spectrophotometric measurements of the absorption peaks of nitrous acid for solutions of different hydrogen ion concentrations allowed the calculation [6] for the $\text{p}K_a$ value for HONO as 2.4 ± 0.1 at 25°C and $\mu = 0.10$ (CF_3COONa). As observed from the results in Table 2, all the measurements led to very close $\text{p}K_a$ values for the HONO. This observation is consistent with the fact that all these peaks correspond to the spectrum of the same species.

There is much controversy in the literature about the $\text{p}K_a$ of HONO, with reported values varying from 2.80 to 5.22 [11–15]. The $\text{p}K_a$ value of 2.4 given in Table 2 is the smallest value reported so far and is one order of magnitude smaller than the first value (3.35) reported [11].

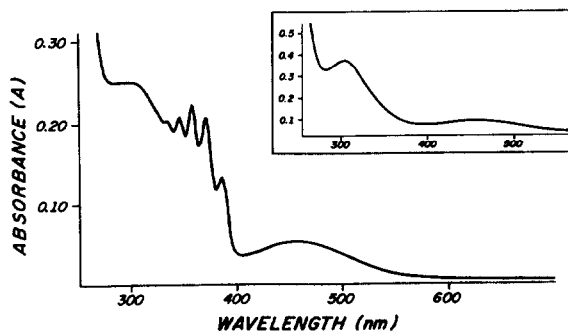


Fig. 3. UV-visible spectrum of the complex $[\text{Ru}(\text{NH}_3)_5\text{NO}]-(\text{PF}_6)_3$ with nitrite impurity. Inset: UV-visible spectrum of the same complex free of nitrite.

TABLE 2

$\text{p}K_a$ values for nitrous acid determined by spectrophotometry ^a

λ (nm)	$\text{p}K_a$
347	2.38 ± 0.08
358	2.42 ± 0.09
372	2.4 ± 0.1
386	2.4 ± 0.1
Mean ^b	2.4 ± 0.1

^a $\mu = 0.10$ ($\text{CF}_3\text{COOH}-\text{CF}_3\text{COONa}$); temperature = $25 \pm 1^\circ\text{C}$.

^b Mean \pm standard deviation ($n = 4$).

Potentiometric measurements in NaNO_2 -HONO solutions allowed the $\text{p}K_a$ value of HONO to be calculate as 2.2 ± 0.1 at 25°C and $\mu = 1.0$ (CF_3COONa). In spite of the difference in ionic strength in the two methods, this value strongly supports the $\text{p}K_a$ value obtained from spectrophotometric data. From the above arguments, it is reasonable to accept a mean $\text{p}K_a$ value of 2.3 ± 0.2 for HONO.

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