

# Spectrophotometric Determination of the Ionization Constants of Aqueous Nitrophenols at Temperatures up to 225 °C

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**Abstract** The UV-visible spectra of aqueous *o*-, *m*-, and *p*-nitrophenol were measured as a function of pH at temperatures from 50 to 225 °C at a pressure of 7 MPa. These were used to determine equilibrium constants for the acid ionization reaction of each isomer. The new results were combined with literature data on the ionization of nitrophenols and used for parameter optimization in the thermodynamic model of Marshall and Franck (J. Phys. Chem. Ref. Data 10:295–304, 1981), to describe the dependence of ionization properties on temperature and pressure. The model yields predictions of the ionization constants for *o*-, *m*-, and *p*-nitrophenol,  $\log_{10} K_a$ , to at least 250 °C and 20 MPa with an estimated uncertainty in  $\log_{10} K_a$  of less than  $\pm 0.06$ .

**Keywords** Ionization constant · Hydrothermal solution · Aqueous acids · *o*-Nitrophenol · *m*-Nitrophenol · *p*-Nitrophenol · UV-visible spectroscopy · Standard thermodynamic properties · Enthalpy of ionization · Entropy of ionization · Heat capacity of ionization · Solvation effects

## 1 Introduction

Nitrophenols constitute a class of volatile organic compounds that is increasingly present in urban as well as in natural environments [1–3]. These compounds are used as raw materials in the chemical, pharmaceutical, dye and herbicide industries, and are also produced in gas-phase oxidation of simple aromatic hydrocarbons. Their toxicity is high even at trace levels, particularly for green plants and for aquatic organisms in surface waters. The thermodynamic data required to calculate the distribution of nitrophenols in environmental models

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have been measured [4, 5], but only at near-ambient conditions. Possible remediation technologies such as steam oxidation require knowledge of the reaction properties of aqueous nitrophenols and nitrophenolate species under a much broader range of conditions. The only experimental results for aqueous nitrophenols that extend to high temperatures are partial molar volumes, which have recently been measured up to 300 °C for all three isomers [6], and ionization constants that have been measured up to 200 °C for *p*-nitrophenol by UV-visible spectroscopy [7]. Accurate ionization constants for the isomers of nitrophenol are particularly useful in spectroscopic studies, because these compounds have been widely used as optical pH indicators at temperatures near 25 °C and have the potential to be used as a tool for pH measurements in hydrothermal solutions. Ionization constants over a wide range of temperatures and pressures are also necessary for the analysis of experimental measurements of all other thermodynamic properties of dilute nitrophenol or nitrophenolate solutions, because the raw data need to be corrected for ionization or hydrolysis, respectively [8].

The purpose of this paper was to determine experimental ionization constants for aqueous *o*-nitrophenol, *m*-nitrophenol and *p*-nitrophenol at elevated temperatures and pressures using UV-visible spectroscopy, and to use the new data along with available literature information to develop an accurate and reliable model for the ionization of nitrophenols under hydrothermal conditions.

## 2 Experimental

### 2.1 Chemicals

All nitrophenols were supplied by Sigma Aldrich (*o*-nitrophenol 98%, *m*-nitrophenol 99%, *p*-nitrophenol  $\geq 99\%$ ) and used as received to prepare stock solutions by mass with deionized water (resistivity = 18 M $\Omega$ ·cm). Stock solutions were prepared immediately before the experiments and stored for maximum five days in the dark to avoid possible decomposition of the solutes. Concentrated (50.1%) solutions of NaOH purchased from Fisher Scientific were used to prepare carbonate-free stock solutions of sodium hydroxide. The molality of the NaOH solutions was determined by titration against a primary standard, potassium hydrogen phthalate (Fisher Scientific, 100.05%). The potassium hydrogen phthalate salt was dried at 110 °C for two hours prior to use. Standard solutions of hydrochloric acid were prepared from ACS reagent-grade concentrated HCl and standardized by titration against a freshly prepared and standardized NaOH solution. The NH<sub>3</sub> solutions were prepared in argon atmosphere to avoid the presence of dissolved CO<sub>2</sub> and standardized by titration against a standard HCl solution. Sodium chloride used for ionic strength adjustment was Fisher Scientific, ACS certified.

### 2.2 Apparatus

The high-temperature, high-pressure spectroscopic flow system used for this work has been described by Trevani et al. [9] and Bulemela et al. [10]. Briefly, a high-pressure liquid chromatography (HPLC) injection system is used to pump solutions through a low-volume platinum cell with sapphire windows that is located in the sample compartment of a Cary 50 UV-visible spectrometer, capable of fast acquisition of digitized spectral data. Deionized water from the pump is injected at a controlled flow rate, sufficient to ensure thermal equilibrium in the pre-heater section of the injection system. Samples of solutions are introduced by means of an HPLC injection loop (2 mm i.d.,  $\sim 16$  cm<sup>3</sup> volume).

### 2.3 Methods

Due to the well-defined and distinct UV-visible absorption spectra of each of the three neutral acidic species and their corresponding nitrophenolate conjugate bases, the nitrophenol isomers can be used as optical pH indicators. In this work, the pH of the nitrophenol solutions was controlled with ammonia/ammonium buffers, prepared from  $\text{NH}_3$  and HCl stock solutions. Sodium chloride was added to maintain the overall ionic strength of the solutions at approximately  $0.2 \text{ mol}\cdot\text{kg}^{-1}$ . The spectra of the acidic form of all nitrophenol isomers were measured in solutions of HCl and NaCl. The spectra of the basic form of *o*-nitrophenol and some of the *p*-nitrophenol samples were obtained in solutions of  $\text{NH}_3$  and NaCl, whereas those of the basic form of *m*-nitrophenol and the other samples of *p*-nitrophenol were measured in solutions of NaOH and NaCl. The buffered solutions of nitrophenols were pumped through the cell at elevated temperatures, at a constant pressure of 7 MPa and at a flow rate of  $1 \text{ cm}^3\cdot\text{min}^{-1}$ . At this flow rate, the solutions were exposed to high temperatures in the pre-heater for  $\sim 2$  min and the residence time in the cell, as measured by the time required to obtain a constant spectrum when water was displaced by the solution, was  $\sim 4$  min. Equilibrium was determined by measuring the flow-rate dependence of the spectra.

Because both the nitrophenol and nitrophenolate species must be present in measurable amounts at the pH of the buffered solutions, measurements can only be performed at temperatures where the ionization constant lies within about a pH unit of the controlled pH [7, 10]. In this study, spectra were obtained for *o*-nitrophenol and *p*-nitrophenol over a range from 100 to 225 °C and, for *m*-nitrophenol, over a range from 50 to 225 °C. At lower temperatures the limitation was set by the pH “window” of the ammonia/ammonium buffers; at temperatures over 225 °C the results showed systematic errors, suggesting that decomposition of the nitrophenols might have taken place.

All spectra were obtained at wavelength intervals of 0.25 nm from 200 nm to 800 nm, at a scan rate  $1200 \text{ nm}\cdot\text{min}^{-1}$ . Five consecutive scans at an interval of four minutes were obtained for each sample and the resulting spectra were averaged to minimize noise. Stopped-flow experiments were conducted at 25 and 225 °C in order to study the stability of nitrophenols in aqueous ammonia/ammonium buffers, hydrochloric acid or sodium hydroxide solutions. In these experiments the flow was stopped for ten minutes and the change of absorbance was measured as a function of time. The only significant change in absorbance of the nitrophenol solutions was observed in the sodium hydroxide base extreme (much less for the ammonia base extreme). However, over the time scale of our measurements the difference in absorbance in the NaOH base extreme was still acceptable (below 2%) except for *o*-nitrophenol at 225 °C where the difference reached 2.8%, and we rather used the ammonia base extreme results for this isomer.

### 2.4 Spectroscopic and Equilibrium Analysis

The total absorbance spectrum of each solution can be treated as a linear combination of the spectra of the acidic and basic forms of nitrophenol, denoted “NphOH” and “NphO<sup>−</sup>”, present at equilibrium:

$$A(\lambda) = (\varepsilon_{\text{NphOH}}(\lambda)bm_{\text{NphOH}} + \varepsilon_{\text{NphO}^-}(\lambda)bm_{\text{NphO}^-})\rho_{\text{solution}} \quad (1)$$

where  $A(\lambda)$  is the absorbance at wavelength  $\lambda$ ,  $\rho_{\text{solution}}$  is the solution density,  $b$  is the path length of the cell and the terms  $m_{\text{NphOH}}$ ,  $\varepsilon_{\text{NphOH}}(\lambda)$  and  $m_{\text{NphO}^-}$ ,  $\varepsilon_{\text{NphO}^-}(\lambda)$  are molalities and molar absorptivities of the indicator in the acidic form and its conjugate base. The

absorptivities for the two species were determined independently each day by measuring the spectrum of nitrophenol in a hydrochloric acid solution, and that of nitrophenolate in a solution of sodium hydroxide or ammonia:

$$\varepsilon_{\text{NphOH}}(\lambda) = \frac{A_{\text{acid}}(\lambda)}{bm_{\text{acid}}\rho_{\text{acid}}}, \quad (2)$$

$$\varepsilon_{\text{NphO}^-}(\lambda) = \frac{A_{\text{base}}(\lambda)}{bm_{\text{base}}\rho_{\text{base}}}. \quad (3)$$

Here,  $m_{\text{acid}}$  and  $m_{\text{base}}$  represent the concentrations of NphOH and NphO<sup>-</sup> in the acidic and basic solutions, respectively. It was assumed that  $m_{\text{acid}}$  is equal to the analytical (“total”) concentration of nitrophenol  $m_{\text{Nitroph}}^{\text{T}}$  in strong acid solution (no dissociation of nitrophenol) and  $m_{\text{base}} = m_{\text{Nitroph}}^{\text{T}}$  in strong base solution (complete dissociation). The densities of acid and base solutions,  $\rho_{\text{acid}}$  and  $\rho_{\text{base}}$ , were assumed equal to  $\rho_{\text{solution}}$ , which is the density of a buffer solution at the same temperature and pressure. Substituting Eqs. 2 and 3 into Eq. 1, and applying the assumptions stated above, leads to

$$A(\lambda) = \left( \frac{A_{\text{acid}}(\lambda)}{m_{\text{acid}}} m_{\text{NphOH}} + \frac{A_{\text{base}}(\lambda)}{m_{\text{base}}} m_{\text{NphO}^-} \right). \quad (4)$$

For a given experimental spectrum, Eq. 4 includes two parameters ( $m_{\text{NphOH}}$  and  $m_{\text{NphO}^-}$ ) that can be determined by a least-squares regression. If the analytical concentration of nitrophenol is known with good accuracy, as it is in our case, mass balance of the indicator in the buffer solution can be applied:  $m_{\text{Nitroph}}^{\text{T}} = m_{\text{NphOH}} + m_{\text{NphO}^-}$ . In this case only one of the concentrations ( $m_{\text{NphOH}}$  or  $m_{\text{NphO}^-}$ ) is treated as a parameter in the regression.

The three components of the buffer solutions, ammonia, water and nitrophenol, are in equilibrium with one another through their ionization reactions. The reactions and corresponding equilibrium constants are given by Eqs. 5–10. For ammonia these are:



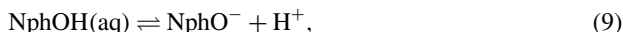
$$K_{\text{b,NH}_3} = \frac{m_{\text{OH}^-} m_{\text{NH}_4^+} \gamma_{\text{OH}^-} \gamma_{\text{NH}_4^+}}{m_{\text{NH}_3} \gamma_{\text{NH}_3}} \quad (6)$$

where the equilibrium constant  $K_{\text{b,NH}_3}$  is given for the hypothetical standard state of a solution at unit molality referenced to infinite dilution (this standard state is used elsewhere in this work). In a similar fashion, the ionization reaction of water is expressed as



$$K_{\text{w}} = \frac{m_{\text{OH}^-} m_{\text{H}^+} \gamma_{\text{OH}^-} \gamma_{\text{H}^+}}{m_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}}. \quad (8)$$

Nitrophenols ionize to nitrophenolate ions



$$K_{\text{a,NphOH}} = \frac{m_{\text{H}^+} m_{\text{NphO}^-} \gamma_{\text{H}^+} \gamma_{\text{NphO}^-}}{m_{\text{NphOH}} \gamma_{\text{NphOH}}}. \quad (10)$$

Besides the equilibrium processes there is a non-reversible dissociation of hydrochloric acid and sodium chloride to complete the system of main reactions.

HCl and NaCl are known to be fully dissociated into  $H^+$ ,  $Na^+$  and  $Cl^-$  ions at our experimental temperatures [11]. The experimental data required for the equilibrium calculations with Eqs. 6, 8, 10 include the equilibrium concentrations of  $m_{NphOH}$  and  $m_{NphO^-}$ , determined from the UV-visible spectra, and the analytical concentrations of ammonia and hydrochloric acid  $m_{NH_3}^T$  and  $m_{HCl}^T$ . In addition, the calculations require values for the equilibrium constants  $K_{b,NH_3}$  and  $K_w$  at the experimental temperatures, and consistent values of activity coefficients. Our data treatment followed a three-step iterative procedure:

1. The molalities of all ionic and non-ionic species were estimated from the known analytical concentrations and simple mass balance, in the first step assuming negligible extent of reactions 5 and 7.
2. The ionic strength, activity coefficients and  $K_{a,NphOH}$  were calculated.
3. The system of Eqs. 6, 8 and 10 was solved for the molalities of  $H^+$ ,  $OH^-$ ,  $NH_4^+$ . The calculation then proceeded back to the previous step. Two to three iterations were enough to obtain stable results.

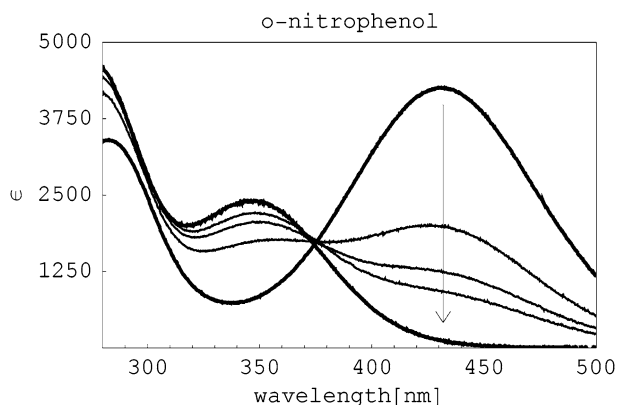
A detailed description of the activity coefficient models which we applied, and the literature sources used for  $K_{b,NH_3}$ ,  $K_w$ , is provided in the next section.

### 3 Results

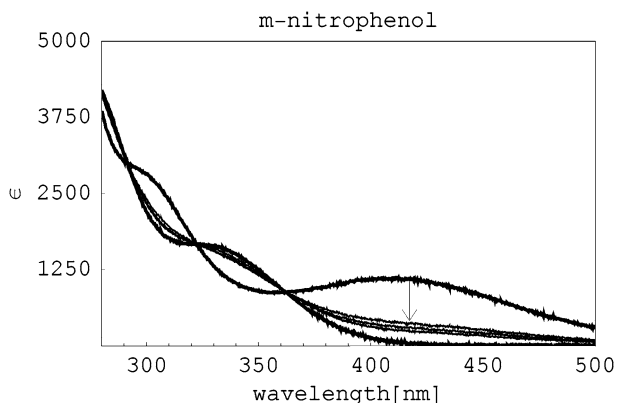
Typical spectra from one set of measurements on each of the three nitrophenol isomers are shown in Figs. 1–3. These were obtained at a temperature of 200 °C and pressure of 7 MPa. Only the prominent absorption bands in the wavelength range 280–500 nm were used for evaluation of the NphOH and NphO<sup>-</sup> concentrations. The spectra of buffer solutions are clearly a linear combination of the spectra of the acid and base extremes, confirming that the ionized and unionized nitrophenol species coexist in the solutions, consistent with the model presented above.

The spectroscopic data were regressed using Eq. 4 with the molalities  $m_{NphOH}$  and  $m_{NphO^-}$  as independent parameters. The results were then compared with the experimental value of  $m_{Nitroph}^T$  and the spectra leading to a difference over 5% in mass balance were excluded from further evaluation. The purpose of this two-parameter fit was only to identify and eliminate spectra for which the uncertainty in solution preparation could affect the output. As a result, 24 data sets (12 for *o*-nitrophenol, none for *m*-nitrophenol and 12 for *p*-nitrophenol) were excluded. Preliminary fits were performed while the experiments were

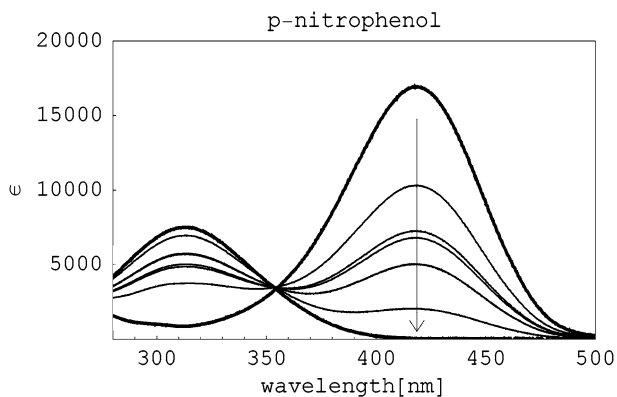
**Fig. 1** Spectra of *o*-nitrophenol at  $t = 200^\circ C$ ,  $p = 7$  MPa.  $\epsilon$  is the absorbance normalized by molality of the indicator, the arrow shows direction of decrease in pH. Bold lines correspond to acid and base extremes



**Fig. 2** Spectra of *m*-nitrophenol at  $t = 200^\circ\text{C}$ ,  $p = 7\text{ MPa}$ .  $\varepsilon$  is the absorbance normalized by molality of the indicator, the *arrow* shows direction of decrease in pH. *Bold lines* correspond to acid and base extremes



**Fig. 3** Spectra of *p*-nitrophenol at  $t = 200^\circ\text{C}$ ,  $p = 7\text{ MPa}$ .  $\varepsilon$  is the absorbance normalized by molality of the indicator, the *arrow* shows direction of decrease in pH. *Bold lines* correspond to acid and base extremes



in progress and the excluded solutions were typically prepared again at similar compositions so that their spectra could be re-measured. The remaining spectra, which met these criteria, were regressed with Eq. 4 using a single parameter ( $m_{\text{NphOH}}$ ), by applying the known value of  $m_{\text{Nitroph}}^{\text{T}}$  and mass balance to calculate  $m_{\text{NphO}^-} = m_{\text{Nitroph}}^{\text{T}} - m_{\text{NphOH}}$ .

Literature values for the ionization constant of ammonia,  $K_{\text{b,NH}_3}$  in Eq. 6, were obtained from the correlation of Hitch and Mesmer [12]. Their equation, denoted as Model I in [12], is formulated for the equilibrium quotient  $Q_{\text{b,NH}_3}$  and includes the activity coefficient product for the ammonia species in KCl solution as a function of ionic strength. The equilibrium constant for water,  $K_{\text{w}}$  in Eq. 8, and activity coefficients in Eqs. 8, 10 were obtained from two alternative approximations:

1. Our first model used the value of  $K_{\text{w}}$  and the activity coefficient product for ionization of water from Sweeton et al. [13]. In Eq. 10 we assumed unity for the activity coefficient of the neutral species,  $\gamma_{\text{NphOH}} = 1$ , and applied Pitzer's formulation of the extended Debye-Hückel limiting law [14] to estimate  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{NphO}^-}$ .
2. In our second model the value of  $K_{\text{w}}$  was taken from the new international formulation [15] and activity coefficient products in Eqs. 8, 10 were assumed to be equal to the value of the activity coefficient product in Eq. 6, which was taken from Hitch and Mesmer [12].

The choice of an activity coefficient model proved to be quite crucial, because the ionic strength of our solutions is rather high, about  $0.19\text{ mol}\cdot\text{kg}^{-1}$ . For comparison, we cite the mean activity coefficients at this ionic strength for univalent ions at  $150^\circ\text{C}$  and 7 MPa from

**Table 1** Experimental values of equilibrium constants for *o*-nitrophenol ionization at  $p = 7$  MPa

$t/^\circ\text{C}$	$m_{\text{NH}_3}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{HCl}}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{Nitroph}}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$I/\text{mol}\cdot\text{kg}^{-1}$	Indicator ratio	$-\log_{10} Q_a$	$-\log_{10} K_a$
100	0.1862	0.1548	0.000178	0.188	2.032	6.40	6.73
150	0.1653	0.0805	0.000096	0.173	1.888	6.26	6.64
150	0.1783	0.1081	0.000095	0.184	1.209	6.24	6.63
150	0.1814	0.1300	0.000218	0.185	0.722	6.25	6.64
150	0.1857	0.1544	0.000188	0.187	0.370	6.25	6.64
175	0.1653	0.0805	0.000096	0.173	0.812	6.25	6.66
175	0.1783	0.1081	0.000095	0.184	0.511	6.24	6.66
200	0.1783	0.1081	0.000095	0.184	0.233	6.23	6.69
200	0.1653	0.0805	0.000096	0.173	0.367	6.24	6.70
200	0.1631	0.0480	0.000089	0.175	0.813	6.25	6.71
225	0.1791	0.0205	0.000108	0.203	1.152	6.28	6.81
225	0.1789	0.0282	0.000106	0.202	0.857	6.25	6.78
225	0.1788	0.0388	0.000099	0.201	0.571	6.26	6.79
225	0.1770	0.0644	0.000117	0.198	0.274	6.26	6.79
225	0.1756	0.1136	0.000102	0.194	0.081	6.28	6.81
225	0.1749	0.1301	0.000101	0.193	0.050	6.30	6.82

various sources: (i) from Pitzer's extended Debye-Hückel law [14]  $\gamma_{\pm} = 0.602$ ; (ii) from Hitch and Mesmer [12] (ammonia ionization)  $\gamma_{\pm} = 0.655$ ; (iii) from Sweeton et al. [13] (water ionization)  $\gamma_{\pm} = 0.640$ ; and (iv) from Archer's equation of state for NaCl [11]  $\gamma_{\pm} = 0.665$ . We note that NaCl is usually the most concentrated electrolyte in our solutions. The differences in predicted activity coefficients transform into a difference in the calculated ionization constants  $K_{a,\text{NphOH}}$ , of up to 0.1  $\text{p}K_{a,\text{NphOH}}$  units between our models 1 and 2. We considered the estimates based on the second approximation to be more physically justified, and used the Hitch and Mesmer activity coefficient model for the evaluation of  $K_{a,\text{NphOH}}$  in all subsequent calculations. Main reasons for this choice were the better agreement of the Hitch and Mesmer model with experimental activity coefficients for species present in our solutions and the requirement of consistency among the activity coefficients of the same species appearing in different equilibrium reactions.

The results are summarized in Tables 1–3 and include the analytical molalities of HCl,  $\text{NH}_3$  and NphOH; ionic strength; the ratio  $m_{\text{NphO}^-}/m_{\text{NphOH}}$  obtained from fitting the spectra; and calculated values of the ionization quotient and ionization constant  $\text{p}Q_{a,\text{NphOH}}$  and  $\text{p}K_{a,\text{NphOH}}$ , respectively [ $\text{p}Q_{a,\text{NphOH}} = \text{p}K_{a,\text{NphOH}} - \log_{10}(\gamma_{\text{H}^+}\gamma_{\text{NphO}^-}/\gamma_{\text{NphOH}})$ ]. Average values of  $\text{p}K_{a,\text{NphOH}}$ , along with their estimated uncertainties, are presented in Table 4 for all nitrophenol isomers as a function of temperature at the 7 MPa isobar. The estimated uncertainties are composed of the standard deviation of the calculated values of  $\text{p}K_{a,\text{NphOH}}$  at each given temperature plus the difference between the average values of  $\text{p}K_{a,\text{NphOH}}$  calculated with nitrophenol concentrations from single-parameter and two-parameter regressions of the spectra. This second contribution to the uncertainty accounts for possible systematic errors in solution preparations and changes in speciation due to possible decomposition of the solute. The two uncertainty contributions are usually comparable and do not exceed 0.03  $\text{p}K_{a,\text{NphOH}}$  units each, leading to total uncertainties of no more than 0.06 units in  $\text{p}K_{a,\text{NphOH}}$ .

**Table 2** Experimental values of equilibrium constants for *m*-nitrophenol ionization at  $p = 7$  MPa

$t/^\circ\text{C}$	$m_{\text{NH}_3}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{HCl}}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{Nitroph}}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$I/\text{mol}\cdot\text{kg}^{-1}$	Indicator ratio	$-\log_{10} Q_a$	$-\log_{10} K_a$
50	0.1832	0.1434	0.000220	0.178	1.485	7.81	8.10
50	0.1823	0.1199	0.000189	0.178	2.803	7.81	8.10
100	0.1820	0.0213	0.000224	0.182	6.443	7.46	7.79
100	0.1820	0.0296	0.000225	0.182	4.626	7.44	7.77
100	0.1823	0.0504	0.000221	0.181	2.383	7.44	7.77
100	0.1818	0.0875	0.000246	0.179	0.990	7.44	7.76
100	0.1813	0.1006	0.000216	0.178	0.745	7.43	7.76
100	0.1823	0.1199	0.000189	0.178	0.496	7.42	7.75
150	0.1815	0.0158	0.000222	0.182	1.909	7.24	7.63
150	0.1820	0.0213	0.000224	0.182	1.379	7.25	7.63
150	0.1820	0.0296	0.000225	0.182	0.961	7.24	7.63
150	0.1823	0.0504	0.000221	0.181	0.499	7.23	7.62
150	0.1818	0.0875	0.000246	0.179	0.207	7.23	7.62
175	0.1815	0.0158	0.000222	0.182	0.871	7.21	7.63
175	0.1820	0.0213	0.000224	0.182	0.617	7.22	7.64
175	0.1820	0.0296	0.000225	0.182	0.455	7.19	7.61
175	0.1823	0.0504	0.000221	0.181	0.228	7.19	7.62
200	0.1815	0.0158	0.000222	0.182	0.454	7.14	7.60
200	0.1820	0.0213	0.000224	0.182	0.322	7.15	7.61
200	0.1820	0.0296	0.000225	0.182	0.237	7.12	7.58
225	0.1815	0.0158	0.000222	0.182	0.240	7.09	7.60
225	0.1820	0.0213	0.000224	0.182	0.174	7.09	7.60
225	0.1819	0.0150	0.000210	0.182	0.254	7.09	7.61

The only experimental values of  $pK_{a,\text{NphOH}}$  for comparison with our results are the ionization constants of *p*-nitrophenol reported by Shin et al. [7] at temperatures up to 200 °C. These were obtained by UV-visible spectroscopy in measurements similar to ours using batch cells, rather than a flow cell. The results agree to within the combined estimated uncertainties, although Shin et al.'s results for  $pK_{a,\text{NphOH}}$  are systematically more positive with increasing temperature until 175 °C. We regard their measurement at 200 °C as suspect, because of the possibility of thermal decomposition, which should be more pronounced in a batch cell due to the much longer exposure times. Possible reasons for the systematic difference between the two studies include the choice of activity coefficients, and approximations used in data treatment. Unfortunately, it is not clear from the Shin et al. paper exactly how the solutions were prepared and what was the target ionic strength, so we could not re-construct their treatment.

## 4 Discussion

### 4.1 Thermodynamic Model

The equilibrium constants presented in Table 4 for reaction 9 can be combined with other thermodynamic data on nitrophenols' ionization taken from the literature. These include



**Table 3** Experimental values of equilibrium constants for *p*-nitrophenol ionization at  $p = 7$  MPa

$t/^\circ\text{C}$	$m_{\text{NH}_3}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{HCl}}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$m_{\text{Nitroph}}^{\text{T}}/\text{mol}\cdot\text{kg}^{-1}$	$I/\text{mol}\cdot\text{kg}^{-1}$	Indicator ratio	$-\log_{10} Q_a$	$-\log_{10} K_a$
100	0.1848	0.1714	0.000151	0.180	1.137	6.24	6.56
100	0.1454	0.1262	0.000102	0.277	2.406	6.20	6.57
100	0.1404	0.1275	0.000163	0.288	1.503	6.22	6.60
150	0.1848	0.1714	0.000151	0.180	0.218	6.07	6.46
150	0.1752	0.1061	0.000102	0.186	1.914	6.05	6.44
150	0.1709	0.0792	0.000105	0.188	3.409	6.05	6.44
150	0.1454	0.1262	0.000102	0.277	0.455	6.04	6.48
150	0.1404	0.1275	0.000163	0.288	0.295	6.05	6.49
150	0.1677	0.0819	0.000122	0.176	3.073	6.05	6.43
150	0.1812	0.1102	0.000097	0.187	1.908	6.04	6.43
150	0.1940	0.1621	0.000091	0.195	0.600	6.03	6.43
175	0.0991	0.0182	0.000110	0.108	6.106	5.99	6.35
175	0.1651	0.0488	0.000121	0.177	3.441	5.97	6.39
175	0.1677	0.0819	0.000122	0.176	1.468	5.99	6.40
175	0.1812	0.1102	0.000097	0.187	0.904	5.99	6.41
200	0.1752	0.1061	0.000102	0.186	0.413	5.98	6.45
200	0.1709	0.0792	0.000105	0.187	0.736	5.98	6.45
200	0.1940	0.1621	0.000091	0.195	0.130	5.96	6.44
200	0.1812	0.1102	0.000097	0.187	0.416	5.97	6.44
200	0.1677	0.0819	0.000122	0.176	0.660	5.98	6.44
200	0.1651	0.0488	0.000121	0.177	1.524	5.98	6.44
225	0.1878	0.0220	0.000082	0.188	2.129	6.00	6.52
225	0.1877	0.0305	0.000090	0.187	1.430	6.01	6.53
225	0.1883	0.0520	0.000076	0.187	0.716	6.02	6.54
225	0.1887	0.0909	0.000074	0.186	0.293	6.02	6.54
225	0.1870	0.1038	0.000081	0.183	0.220	6.02	6.53
225	0.1870	0.1230	0.000078	0.183	0.144	6.01	6.53

$K_{a,\text{NphOH}}$  (denoted  $K_a$  in the following discussion) for all nitrophenols at 25 °C and 0.1 MPa by Judson and Kilpatrick [16];  $K_a$  for *m*-nitrophenol from 5 to 50 °C at 0.1 MPa by Robinson and Peiperl [17];  $K_a$  for *p*-nitrophenol from 25 to 200 °C at  $p_{\text{sat}}$  by Shin et al. [7]; and data for the pressure- and temperature-derivatives of the ionization constant, which are available only at 25 °C and 0.1 MPa. These are the standard partial molar enthalpies of ionization  $\Delta H_a^\circ$  for all the nitrophenol isomers [18] and for *p*-nitrophenol [19]; standard partial molar volumes of ionization  $\Delta V_a^\circ$  for *m*-nitrophenol and *p*-nitrophenol [20, 21]; standard partial molar heat capacities of ionization  $\Delta C_{p,a}^\circ$  for *m*-nitrophenol and *p*-nitrophenol [20]. These experimental results are sufficient to allow the development of a comprehensive model describing the changes of  $\text{p}K_a$  for each isomer of nitrophenol with temperature and pressure. Values of the standard state parameters at 25 °C from the literature are summarized in Table 5.

Several models were evaluated for this purpose. Some of the “equations of state” for standard thermodynamic properties used in geochemistry of hydrothermal solutions are suitable [22, 23], as are recent models based on Fluctuation Solution Theory [24]. We have selected

**Table 4** Experimental values for  $pK_a$  of nitrophenols as a function of temperature at  $p = 7$  MPa

$t/^\circ\text{C}$	<i>o</i> -nitrophenol $pK_a$	<i>m</i> -nitrophenol $pK_a$	<i>p</i> -nitrophenol $pK_a$
50	–	$8.10 \pm 0.02^*$	–
100	$6.73 \pm 0.04$	$7.77 \pm 0.03$	$6.58 \pm 0.06$
150	$6.64 \pm 0.04$	$7.63 \pm 0.02$	$6.45 \pm 0.05$
175	$6.66 \pm 0.05$	$7.62 \pm 0.03$	$6.39 \pm 0.06$
200	$6.70 \pm 0.03$	$7.60 \pm 0.03$	$6.44 \pm 0.03$
225	$6.80 \pm 0.03$	$7.61 \pm 0.04$	$6.53 \pm 0.02$

\* Experimental uncertainty  $\sigma$  is calculated as a sum of the standard deviation of experimental  $pK_a$  and a difference of average  $pK_a$  obtained from fitting the spectra, Eq. 4, with one parameter or with two parameters

**Table 5** Literature values for the standard state thermodynamic properties of aqueous isomers of nitrophenol at  $25^\circ\text{C}$  and 0.1 MPa

	<i>o</i> -nitrophenol	<i>m</i> -nitrophenol	<i>p</i> -nitrophenol	Reference
$K_a \times 10^{10}$	$589 \pm 30^*$	$44.7 \pm 2$	$724 \pm 30$	[16]
$\Delta H_a^\circ / (\text{J}\cdot\text{mol}^{-1})$	$19480 \pm 500$	$19690 \pm 500$	$19660 \pm 500$	[18]
$\Delta S_a^\circ / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	–72.8	–94.1	–70.7	from $K_a$ and $\Delta H_a^\circ$
$\Delta C_{p,a}^\circ / (\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$	–	$-112 \pm 2$	$-95.4 \pm 2$	[20]
$\Delta V_a^\circ / (\text{cm}^3\cdot\text{mol}^{-1})$	–	$-13.6 \pm 0.4$	$-11.9 \pm 0.4$	[20]

\* Experimental uncertainty  $\sigma$  as reported in the original publications or estimated in this work

the “density” model proposed originally by Marshall and Franck [23] for the ionization constant of water, and developed further by Mesmer et al. [25, 26]. This is satisfactory for our purpose, because it is simple and can be easily used for simultaneous regression of data on various properties of ionization. For  $K_a$  the expression is

$$\ln K_a = -pK_a \ln 10 = -\Delta G_a^\circ / (RT) = a + b/T + c/T^2 + d/T^3 + (e + f/T + g/T^2) \ln \rho_w \quad (11)$$

where  $pK_a = -\log_{10} K_a$ ;  $\Delta G_a^\circ$  is the standard partial molar Gibbs energy of ionization;  $\rho_w$  is the density of water ( $\text{kg}\cdot\text{m}^{-3}$ );  $T$  is the thermodynamic temperature (K) and  $a$ – $g$  are model parameters. Other standard partial molar properties of ionization are obtained by appropriate derivations of this equation

$$\Delta H_a^\circ = -R(b + 2c/T + 3d/T^2 + \ln \rho_w (f + 2g/T) + \alpha_w (eT^2 + fT + g)), \quad (12)$$

$$\Delta S_a^\circ = (\Delta H_a^\circ - \Delta G_a^\circ) / T, \quad (13)$$

$$\Delta C_{p,a}^\circ = -R \left( -2c/T^2 - 6d/T^3 - 2g/T^2 \ln \rho_w + \alpha_w (2eT - 2g/T) + \left( \frac{\partial \alpha_w}{\partial T} \right)_p (eT^2 + f + g/T) \right), \quad (14)$$

$$\Delta V_a^\circ = -R(eT + f + g/T) \kappa_w \quad (15)$$

**Table 6** Parameters of Eq. 11 for nitrophenols

Solute	<i>a</i>	<i>b</i> /K	<i>c</i> /K <sup>2</sup>	<i>d</i> /K <sup>3</sup>	<i>e</i>	<i>f</i> /K	<i>g</i> /K <sup>2</sup>
<i>o</i> -nitrophenol	−82.128	0	−3.8341 × 10 <sup>5</sup>	0	10.106	0	0
<i>m</i> -nitrophenol	−91.888	−2220.4	−72678	0	11.720	0	0
<i>p</i> -nitrophenol	−110.51	6400.6	0	0	14.899	−1307.4	0

where  $\Delta S_a^\circ$  is the standard partial molar entropy of ionization,  $\alpha_w = \frac{-1}{\rho_w} \left( \frac{\partial \rho_w}{\partial T} \right)_p$  and  $\kappa_w = \frac{1}{\rho_w} \left( \frac{\partial \rho_w}{\partial p} \right)_T$  are the thermal expansivity and isothermal compressibility of water solvent, respectively. The properties of water can be calculated from the equation of state by Wagner et al. [27], which is recommended by the International Association for the Properties of Water and Steam (IAPWS).

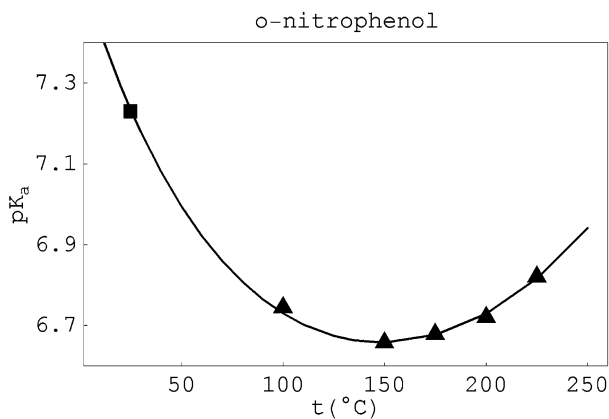
The experimental values of  $pK_a$  for the ionization of each nitrophenol isomer in Table 4, and the low-temperature literature values cited above, were subjected to a simultaneous weighted fit with the objective function

$$F = \sum_{i=1}^O \left( \frac{pK_a^{\text{exp}} - pK_a^{\text{calc}}}{\sigma pK_a} \right)_i^2 + \sum_{j=1}^P \left( \frac{\Delta H_a^{\circ, \text{exp}} - \Delta H_a^{\circ, \text{calc}}}{\sigma \Delta H_a^\circ} \right)_j^2 + \sum_{k=1}^Q \left( \frac{\Delta C_{p,a}^{\circ, \text{exp}} - \Delta C_{p,a}^{\circ, \text{calc}}}{\sigma \Delta C_{p,a}^\circ} \right)_k^2 + \sum_{l=1}^R \left( \frac{\Delta V_a^{\circ, \text{exp}} - \Delta V_a^{\circ, \text{calc}}}{\sigma \Delta V_a^\circ} \right)_l^2 \quad (16)$$

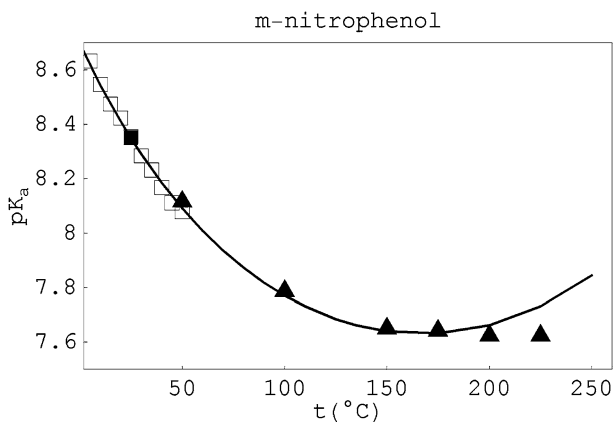
where exp and calc stand for experimental and calculated values, respectively, and  $\sigma X$  is the estimated experimental uncertainty. The experimental values for  $K_a$  of *p*-nitrophenol reported by Shin et al. [7] were not included in the regression. The term  $\sigma pK_a$  was used as in Table 4,  $\sigma \Delta H_a^\circ$  was set to 500 J·mol<sup>−1</sup>,  $\sigma \Delta C_{p,a}^\circ$  to 2 J·K<sup>−1</sup>·mol<sup>−1</sup> and  $\sigma \Delta V_a^\circ$  to 0.4 cm<sup>3</sup>·mol<sup>−1</sup> in the regressions. A statistical *t*-test at 95% confidence level was applied on the resulting parameters and the first coefficient that was not statistically significant was excluded from the fit. The regression was repeated until the absolute values of all parameters were larger than their 95% confidence intervals. The number of significant parameters was found to range from three (*o*-nitrophenol) to four (*m*- and *p*-nitrophenol) and the description of experimental data was well within the estimated uncertainties in all cases. The resulting parameters of Eq. 11 for the three nitrophenols are reported in Table 6. Figures 4–6 provide a graphical comparison of the experimental values of  $K_a$  with the predictions of Eq. 11 along the saturation line for water. Data reported in this work that correspond to the pressure of 7 MPa were corrected to  $p_{\text{sat}}$  by using the model (Eq. 11). The calculated pressure corrections were less than 0.03  $pK_a$  units at all temperatures. Eq. 11 deviates from our experimental results by no more than 0.04 units in  $pK_a$  (the standard error is  $\pm 0.01$ – $0.02$   $pK_a$  units).

A thermodynamic test was applied to check the consistency of data sets on  $K_a$  at elevated temperatures with the other experimental data for the ionization of *p*-nitrophenol that correspond to standard reference conditions ( $T_r = 25^\circ\text{C}$  and  $p_r = 0.1$  MPa). It is well known that equilibrium constants at saturation pressure can be calculated with good accuracy as a function of temperature to at least 100 °C using the values of  $K_a$ ,  $\Delta H_a^\circ$  and  $\Delta C_{p,a}^\circ$  at 25 °C and 0.1 MPa. As an example, this approximation was recently used with success for calculating the thermodynamic properties of (alkyl)phenols and (alkyl)anilines [28] that are similar

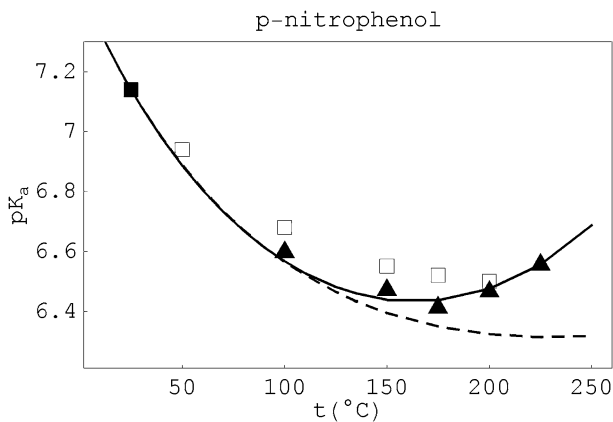
**Fig. 4** Ionization constant ( $pK_a$ ) of *o*-nitrophenol as a function of temperature at  $p_{\text{sat}}$ . Predictions of Eq. 11 (full line). Experimental data: Judson and Kilpatrick [16] (squares); this work, corrected from  $p = 7$  MPa to  $p_{\text{sat}}$  (triangles)



**Fig. 5** Ionization constant ( $pK_a$ ) of *m*-nitrophenol as a function of temperature at  $p_{\text{sat}}$ . Predictions of Eq. 11 (full line). Experimental data: Judson and Kilpatrick [16] (squares); Robinson and Peiperl [17] (open squares); this work, corrected from  $p = 7$  MPa to  $p_{\text{sat}}$  (triangles)



**Fig. 6** Ionization constant ( $pK_a$ ) of *p*-nitrophenol as a function of temperature at  $p_{\text{sat}}$ . Predictions of Eq. 11 (full line); predictions from a thermodynamic integration, Eq. 18 (dashed line). Experimental data: Judson and Kilpatrick [16] (squares); Shin et al. [7] (open squares); this work, corrected from  $p = 7$  MPa to  $p_{\text{sat}}$  (triangles)



solutes to nitrophenols. The calculation is based on simple thermodynamic integration

$$\Delta G_a^\circ[T] = \Delta G_a^\circ[T_r] + (T_r - T) \Delta S_a^\circ[T_r] + \int_{T_r}^T \Delta C_{p,a}^\circ dT - T \int_{T_r}^T \Delta C_{p,a}^\circ d \ln T. \quad (17)$$

The functional dependence on temperature was added to Eq. 17 and to the following for clarity. Assuming a constant value of  $\Delta C_{p,a}^{\circ}$  in Eq. 17 leads to

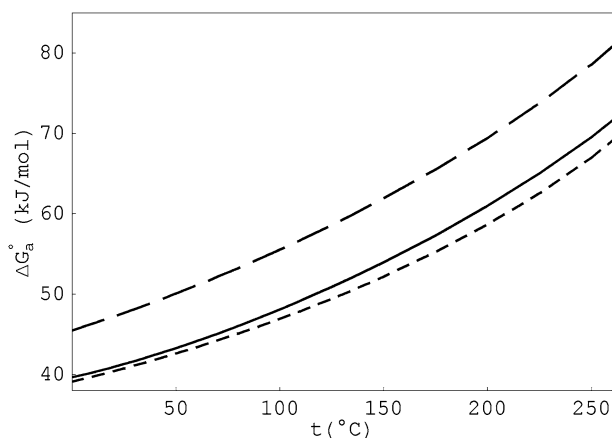
$$\Delta G_a^{\circ}[T] = \Delta H_a^{\circ}[T_r] + (T - T_r) \Delta C_{p,a}^{\circ}[T_r] - T (\Delta S_a^{\circ}[T_r] + \Delta C_{p,a}^{\circ}[T_r] \ln(T/T_r)) \quad (18)$$

which is the integrated form of van't Hoff equation. The ionization properties for *p*-nitrophenol at 25 °C are available from reliable sources in the literature [16, 18, 20], and these allow us to compare the predictions from the van't Hoff equation with the data and models at elevated temperatures. The predictions of Eq. 18 in Fig. 6 show excellent agreement with calculations using Eq. 11 up to 100 °C, and are more negative than the experimental value reported here and corrected to  $p_{\text{sat}}$  at 100 °C by only 0.03 p*K*<sub>a</sub> units. The deviation between the extrapolated value from Eq. 18 and the measured value reported by Shin et al. [7] is larger, 0.12 p*K*<sub>a</sub> units at 100 °C, but still lies within the combined experimental uncertainties.

## 4.2 Solvation Effects

The effects of temperature and pressure on solvation are reflected in the standard state thermodynamic properties derived from the model using Eqs. 12–15. The calculated values for the standard Gibbs energy of ionization,  $\Delta G_a^{\circ}$ , are plotted in Fig. 7 and listed in Table 7 in terms of p*K*<sub>a</sub>. The values for the standard enthalpy and entropy of ionization,  $\Delta H_a^{\circ}$  and  $\Delta S_a^{\circ}$ , are listed in Tables 8 and 9 and plotted in Figs. 8 and 9. Values for the standard partial molar heat capacity and volume of ionization,  $\Delta C_{p,a}^{\circ}$  and  $\Delta V_a^{\circ}$ , are plotted in Figs. 10 and 11. In our judgment, the database from which the model parameters were fitted is too limited to permit realistic estimates of the uncertainties associated with these calculated derivative functions by error propagation analysis. Instead, approximate uncertainty limits were estimated from the relative error of model predictions from experimental p*K*<sub>a</sub> data, and considering the magnification of uncertainty upon derivation to determine the uncertainties in the other properties. This leads to estimated uncertainties in  $\Delta H_a^{\circ}$  of 0.4–0.8 kJ·mol<sup>-1</sup>;  $\Delta S_a^{\circ}$ , 3–6 J·K<sup>-1</sup>·mol<sup>-1</sup>;  $\Delta C_{p,a}^{\circ}$ , 10–40 J·K<sup>-1</sup>·mol<sup>-1</sup>; and  $\Delta V_a^{\circ}$ , 0.4–4 cm<sup>3</sup>·mol<sup>-1</sup> where the lower limits are for 25 °C and the upper limits for 200 °C. The large uncertainty in  $\Delta V_a^{\circ}$  at elevated temperatures arises because, with the exception of the volumetric data at 25 °C, the calculated values are entirely dependent on parameters determined by fitting the temperature dependence, rather than the pressure dependence of p*K*<sub>a</sub>.

**Fig. 7** Standard partial molar Gibbs energy of ionization calculated from Eq. 11 with parameters from Table 6 at  $p_{\text{sat}}$ . Full line: *o*-nitrophenol; long-dashed line: *m*-nitrophenol; short-dashed line: *p*-nitrophenol



**Table 7**  $pK_a$  calculated from Eq. 11 with parameters from Table 6 at  $p_{\text{sat}}$  and at 20 MPa

$t/^\circ\text{C}$	<i>o</i> -nitrophenol		<i>m</i> -nitrophenol		<i>p</i> -nitrophenol	
	$p_{\text{sat}}$	20 MPa	$p_{\text{sat}}$	20 MPa	$p_{\text{sat}}$	20 MPa
25	7.23	7.20	8.35	8.30	7.14	7.10
50	7.00	6.96	8.09	8.05	6.89	6.85
100	6.73	6.69	7.77	7.72	6.57	6.52
150	6.66	6.61	7.64	7.58	6.44	6.38
200	6.73	6.66	7.66	7.58	6.47	6.39
250	6.94	6.85	7.84	7.74	6.69	6.57

**Table 8** Standard partial molar enthalpy of ionization (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) calculated from Eq. 12 with parameters from Table 5 at  $p_{\text{sat}}$  and at 20 MPa

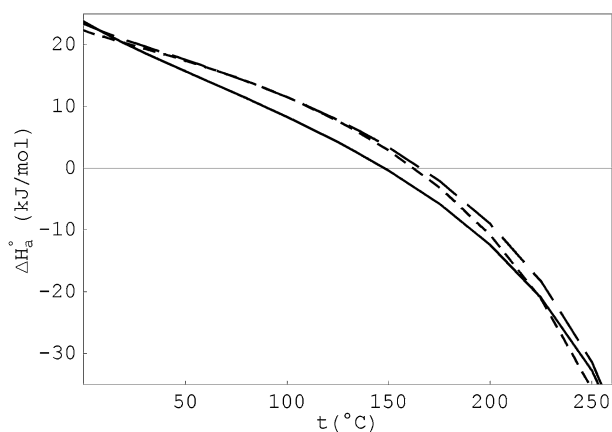
$t/^\circ\text{C}$	<i>o</i> -nitrophenol		<i>m</i> -nitrophenol		<i>p</i> -nitrophenol	
	$p_{\text{sat}}$	20 MPa	$p_{\text{sat}}$	20 MPa	$p_{\text{sat}}$	20 MPa
25	19.46	19.30	20.28	20.10	19.84	19.76
50	15.72	15.74	17.55	17.57	17.43	17.54
100	8.31	8.68	11.52	11.95	11.51	12.03
150	-0.36	0.60	5.42	4.54	2.90	4.15
200	-12.42	-10.14	-9.02	-6.37	-10.80	-7.90
250	-32.81	-27.04	-31.41	-24.72	-35.77	-28.47

**Table 9** Standard partial molar entropy of ionization (in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) calculated from Eq. 13 with parameters from Table 6 at  $p_{\text{sat}}$  and at 20 MPa

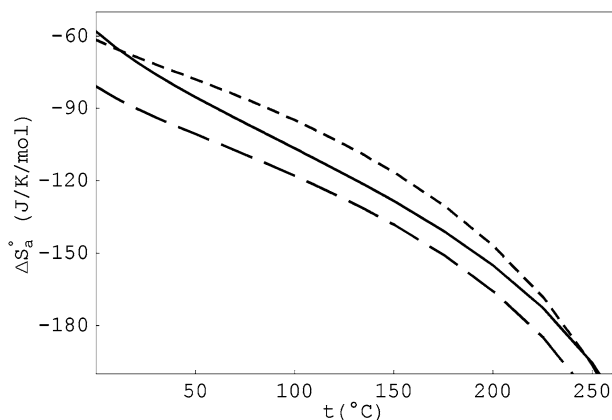
$t/^\circ\text{C}$	<i>o</i> -nitrophenol		<i>m</i> -nitrophenol		<i>p</i> -nitrophenol	
	$p_{\text{sat}}$	20 MPa	$p_{\text{sat}}$	20 MPa	$p_{\text{sat}}$	20 MPa
25	-73.2	-73.0	-92.8	-91.6	-70.2	-69.7
50	-85.3	-84.5	-100.6	-99.7	-77.9	-76.8
100	-106.6	-104.8	-117.9	-115.8	-94.9	-92.6
150	-128.3	-125.1	-138.2	-134.4	-116.4	-112.3
200	-155.1	-149.0	-165.8	-158.7	-146.8	-139.1
250	-195.6	-182.8	-210.2	-195.4	-196.4	-180.2

There are significant differences in the properties of the three isomers at room temperature, as listed in Table 5. These have been attributed to the electron-withdrawing effects of the nitro group, which stabilize the  $\text{NphO}^-$  anion, and to solvation effects that manifest themselves in the entropy, heat capacity and volume of ionization. Intra-molecular hydrogen-bonding of the phenolic group in *o*-nitrophenol may also be a factor. The electron-withdrawing effects are larger for the *o*- and *p*-isomers than for *m*-nitrophenol (see, for example, Dewick [29]). Fernandez and Hepler [18] have noted that *m*-nitrophenol is a weaker acid than *o*- or *p*-nitrophenol at room temperature because its entropy of ionization is significantly more negative, and *not* because of a more endothermic enthalpy of ionization (see Table 5). Apparent molar volume and heat capacity measurements on *p*- and *m*-nitrophenol

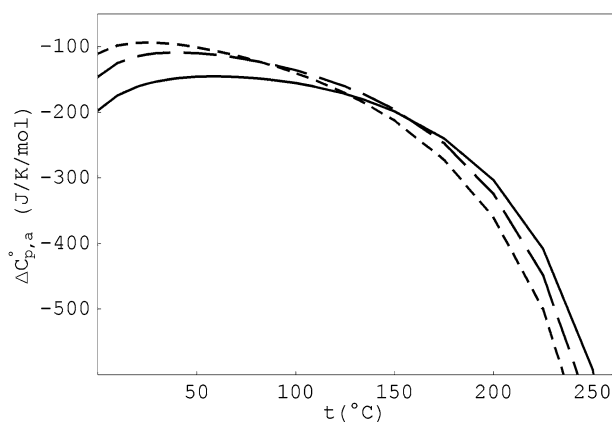
**Fig. 8** Standard partial molar enthalpy of ionization calculated from Eq. 12 with parameters from Table 6 at  $p_{\text{sat}}$ . *Full line:* *o*-nitrophenol; *long-dashed line:* *m*-nitrophenol; *short-dashed line:* *p*-nitrophenol



**Fig. 9** Standard partial molar entropy of ionization calculated from Eq. 13 with parameters from Table 6 at  $p_{\text{sat}}$ . *Full line:* *o*-nitrophenol; *long-dashed line:* *m*-nitrophenol; *short-dashed line:* *p*-nitrophenol

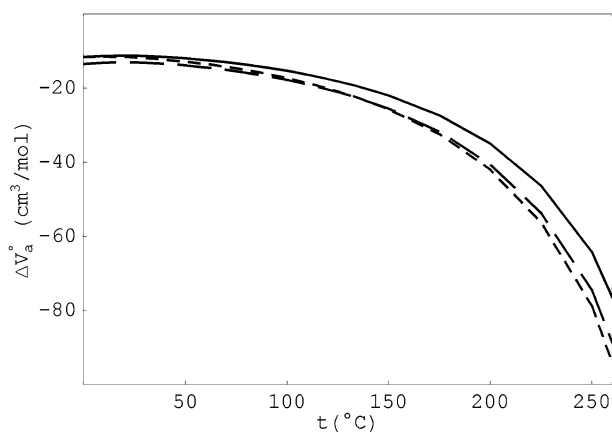


**Fig. 10** Standard partial molar heat capacity of ionization calculated from Eq. 14 with parameters from Table 6 at  $p_{\text{sat}}$ . *Full line:* *o*-nitrophenol; *long-dashed line:* *m*-nitrophenol; *short-dashed line:* *p*-nitrophenol



and their sodium salts [20, 21] suggest that this effect arises primarily because of differences in solvation on the uncharged species, with  $V^\circ(p\text{-NphOH}) < V^\circ(m\text{-NphOH})$ , and  $C_p^\circ(p\text{-NphOH}) < C_p^\circ(m\text{-NphOH})$ . These observations are all consistent with solvation ef-

**Fig. 11** Standard partial molar volume of ionization calculated from Eq. 15 with parameters from Table 6 at  $p_{\text{sat}}$ . Full line: *o*-nitrophenol; long-dashed line: *m*-nitrophenol; short-dashed line: *p*-nitrophenol



fects in which water is more tightly bound by the *o*- and *p*-isomers than by the *m*-isomer at 25 °C.

Although the relative positions of the Gibbs energies of ionization of the isomers do not change with increasing temperature, as illustrated in Fig 7, there are changes in the contributions of the standard state enthalpy and entropy. These are plotted in Figs. 8 and 9. While both  $\Delta H_a^o$  and  $\Delta S_a^o$  become increasingly negative with increasing temperature, the entropic term is the major contribution to the Gibbs energy of ionization above about 200 °C, i.e., the absolute values of  $T \Delta S_a^o \gg \Delta H_a^o$ . This effect has been observed for a great many acids and bases [25, 30]. It arises from the long-range polarization of water by the charged anion and hydrated proton, an effect which becomes much more important at elevated temperatures as the dielectric constant of water decreases. Whereas the relative order of  $\Delta H_a^o$  and  $\Delta S_a^o$  for the three isomers at temperatures above 200 °C is the same as that at room temperature,  $\Delta S_a^o(m\text{-NphOH}) < \Delta S_a^o(p\text{-NphOH}) \approx \Delta S_a^o(o\text{-NphOH})$ , the relative position of the ortho-isomer at intermediate temperatures changes significantly, so that  $\Delta S_a^o(m\text{-NphOH}) < \Delta S_a^o(o\text{-NphOH}) < \Delta S_a^o(p\text{-NphOH})$ . This effect, which lies just outside the combined estimates of uncertainty, may reflect the competing effects of localized hydrogen bonding around the uncharged species and solvent polarization effects. Temperatures in the range  $t \approx 100$  to 250 °C are typically considered a transition region, in which water behaves like a “normal” hydrogen-bonded solvent, so that both effects are often of similar magnitude.

Plots of the standard partial molar heat capacity and volume functions,  $\Delta C_{p,a}^o$  and  $\Delta V_a^o$ , in Figs. 10 and 11 also reflect this behavior. Both functions show a tendency that is associated with solvent polarization effects. The figures clearly show the transition with increasing temperature from the distinctly different experimental values for each isomer at ambient temperatures, through a maximum, towards the large negative values associated with solvent polarization in the near-critical region [25, 30]. Because  $\Delta C_{p,a}^o$  and  $\Delta V_a^o$  are derivative functions, there is considerable uncertainty in the high-temperature values, as calculated from Eqs. 10 and 11, so that the results for the three isomers above  $\sim 150$  °C agree to within the rather large combined error limits. Measurements are under way to determine the standard partial molar heat capacity and volume of each isomer and its conjugate base, in order to confirm whether significant differences do exist at elevated temperatures.



**Table 10** Parameters of Eq. 19 for nitrophenols

Solute	$x_1/K^{-1}$	$x_2$	$x_3/K$	$x_4/K^2 \times 10^{-6}$	$x_5$
<i>o</i> -nitrophenol	0.11047	695.94	−37601	2.3669	−109.20
<i>m</i> -nitrophenol	0.12811	805.64	−42643	2.5834	−126.64
<i>p</i> -nitrophenol	0.14246	885.45	−46442	2.7552	−139.71

## 5 Conclusions

Measured high-temperature ionization constants of aqueous nitrophenols were combined with other standard state properties on ionization reactions retrieved from the literature. The databases were used for parameterization of the thermodynamic model, Eq. 11, describing the evolution of  $pK_a$  and other ionization functions with temperature and pressure. Applying Eq. 11 and its derivatives (Eqs. 12–15) is straightforward, but requires at the input thermodynamic properties of water, calculated from some fundamental equation of state. In typical applications, the knowledge of  $pK_a$  is needed just along the saturation line of water. At these conditions, some empirical function may be used such as:

$$pK_a = x_1 T + x_2 + x_3/T + x_4/T^2 + x_5 \ln T. \quad (19)$$

Parameters  $x_1$ – $x_5$  in Eq. 19 were adjusted for all nitrophenols so that calculations with Eq. 19 are practically identical to the results of Eq. 11 at  $p_{\text{sat}}$  (maximum difference was below 0.005  $pK_a$  units). Obtained parameters of Eq. 19 are provided in Table 10 and can be used for easy calculations of the ionization constants of *o*-, *m*- and *p*-nitrophenol as a function of temperature and at the saturation pressure.

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