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Spectrophotometric Determination of Equilibrium Constants and Speciation of Aqueous Systems over a Wide Range of Temperature and Pressure

Report of the PhD Thesis

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Title:	Spectrophotometric Determination of Equilibrium Constants and Speciation of Aqueous Systems over a Wide Range of Temperature and Pressure
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Abstrakt

Cílem této práce bylo určení termodynamických veličin, konkrétně reakčních rovnovážných konstant, pro dva vybrané vodné systémy za vysokých teplot a tlaků s využitím UV-vis průtokové spektrofotometrie a termodynamického modelování. Systémy zvolené ke studiu jsou významné z hlediska průmyslových aplikací popř. ochrany životního prostředí, ale i z hlediska fundamentálního výzkumu.

Do první části byly zařazeny vodné roztoky nitrofenolů, všech tří izomerů (o-, m- a p-). Nejprve byla proměřena jejich UV-vis spektra jako funkce pH při teplotách od 50 do 225 °C a tlaku 7 MPa, spektra pak byla použita ke stanovení rovnovážných konstant ionizační reakce jednotlivých izomerů. Nové výsledky spolu s literárními údaji o ionizaci nitrofenolů posloužily k parametrizaci termodynamického modelu Marshalla a Francka [Marshall and Franck, 1981] , který popisuje závislost ionizačních veličin na teplotě a tlaku. Navržený model poskytuje predikce ionizačních konstant o-, m- a p-nitropfenolu, $\log_{10} \mathrm{K_a}$, přinejmenším do 250 °C a do 20 MPa s odhadem chyby $\log_{10} \mathrm{K_a}$ menší než ± 0.06.

Ve druhé části byla UV-vis spektrofotometrie užita ke studiu reakčních konstant slučovacích reakcí komplexů dvojmocné mědi a chloridů v roztocích LiCl s proměnnou koncentrací, od nízkých až k vysokým koncentracím. Měření byla provedena při třech teplotách 100, 150 a 200°C a tlaku 9 MPa. Pomocí analýzy hlavních komponent byl stanoven počet komplexů chloridů a mědi potřebný k popisu variace spektra s proměnnou koncentrací chloridů při každé teplotě. V dalším kroku byla vyhodnocena speciace v roztoku a příslušné molární absorpční koeficienty bez předpokladu chemických reakcí v roztoku probíhajících. Do finálního modelu byly kromě experimentálních informací zahrnuty termodynamické vazné podmínky, konkrétně slučovací reakce uvažovaných komplexů, asociační reakce elektrolytů v roztoku (LiCl, HCl) a odpovídající aktivitní koeficienty. Optimalizovanými parametry modelu speciace byly logaritmy rovnovážných slučovacích konstant komplexů mědi a chloridů, získané nelineární regresí naměřených spektrálních dat.

Summary

The aim of this work was to determine thermodynamic properties, in particular reaction equilibrium constants, of two selected systems at high temperatures and pressures using UV-visible flow spectroscopy and appropriate thermodynamic modeling. The selected systems are important either from the perspective of industrial application or environmental concern, but also from the fundamental point of view.

In the first part of this study 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 [Marshall and Franck, 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, $\log_{10}\mathrm{K_a}$, to at least 250°C and 20 MPa with an estimated uncertainty in $\log_{10}\mathrm{K_a}$ of less than ±0.06.

In the second part the UV-visible spectrophotometry was used to study the formation of $\mathrm{Cu^{II}}$-chloride complexes in LiCl brines up to very high chloride concentrations, at temperatures of 100, 150 and 200°C and at a pressure of 9 MPa. The number of $\mathrm{Cu^{II}}$-chloride complexes that are necessary to account for the variation of the spectra with varying chloride concentration at each temperature was estimated by Principal Component Analysis. The molar absorptivity coefficients and concentrations of each complex were then determined without any assumption about the chemistry of the system other than the number of absorbing species present in the solution. Subsequently, the molar absorptivity coefficients and concentrations were integrated with independent experimental evidence to develop a thermodynamic speciation model, where the logarithms of the equilibrium constants for $\mathrm{Cu^{II}}$-chloride formation reactions were fitted to the data using a non-linear least-squares approach.

Keywords

Ionization constant • Nitrophenols • UV-visible spectroscopy • Standard thermodynamic properties • Copper-chloride complexes • Colorimetric pH indicator • High-temperature

1 Introduction

Thermodynamic properties of aqueous solutions at high temperatures and pressures are required for modeling of a variety of environmental and industrial processes such as hydrothermal reactions during mineral formation, mining and processing of oil in contact with deep-underground water or seawater, chemical industry when water is used as a solvent, remediation processes in saturated soils and/or water bodies, energy generation by power cycles, etc. Therefore a lot of effort has been devoted to this area over the last decades, both on experimental and theoretical levels.

Experimental high-temperature studies of solution properties improved in quality and reliability particularly with the advance of modern through-flow systems, widely used now in calorimetry and densimetry. Other often applied experimental techniques in this field include potentiometry, conductometry, isopiestic measurements, vapor-liquid equilibrium experiments, some spectroscopic methods etc.

When interpreting the measured results it is necessary to know exact composition of the system of interest in every moment at which the data are recorded. If any reaction takes place in the solution, it is necessary to have sufficient information about this process. When the reaction is not controlled kinetically, the needed information includes its equilibrium constant and the values of the activity coefficients of the reacting species. Spectroscopic methods (UV-visible, NIR, Raman) represent relatively simple and efficient method that can be used to quantify the actual composition of the reaction-bearing solution. Spectroscopic measurements combined with a suitable thermodynamic model for activity coefficients of the present species lead to the values of equilibrium constants of reactions taking place in the system, which can be used then for various modeling purposes that include speciation in the aqueous media.

We have applied in this work the high-temperature, high-pressure, flow-through UV-visible spectroscopic technique on selected reacting aqueous systems. An important part of this study is thermodynamic modeling of infinite dilution as well as finite concentration effects in the solutions, which was necessary for appropriate elucidation of the target properties (reaction equilibrium constants). Motivation for the particular choice of our systems is explained in the following sections. Briefly, the selected systems are important either from the perspective of industrial application or environmental concern, but also from the fundamental point of view.

Two groups of aqueous systems were studied. The first group included three isomeric nitrophenols and nitrophenolate ions that are considered as key compounds for group contribution methods, they are also widespread pollutants and can be used as spectroscopic pH indicators at high temperatures and pressures. The objective of this part of the work was to determine thermodynamic properties of ionization for three nitrophenol isomers in a wide range of conditions.

The second system we have studied is aqueous solutions of chlorides up to high concentrations and their complexes with copper(II). Copper-chloride solutions are a part of thermochemical cycle for hydrogen production in the "Generation IV" Super-Critical-Water-Cooled Reactor design that is now in technology development and optimization phase. The aim here was to determine equilibrium constants of formation for aqueous mononuclear copper(II) chlorocomplexes at high temperatures to complement the existing low-temperature results and provide a basis for the development of a complex thermodynamic model.

2 Nitrophenols Ionization

2.1 Objectives

The purpose of this study was to develop a model of speciation in aqueous solutions of nitrophenols in a wide range of temperature and pressure. Derived thermodynamic properties of ionization for aqueous nitrophenols can be then used in various applications e.g. in environmental modeling, in spectroscopic studies or for interpretation of other thermodynamic data measured on these systems (densimetric, calorimetric etc.). Our main intention is to use the ionization properties in a subsequent project aimed at the extension of high-temperature group contribution method by nitro- functional group. Presented study proceeded in two steps:

1. Experimental determination of ionization constants for aqueous o-nitrophenol, m-nitrophenol and p-nitrophenol at elevated conditions using UV-visible spectroscopy.
2. Using the new data along with available literature information for development of accurate and reliable model for the ionization of nitrophenols at high temperatures and pressures.

2.2 Nitrophenols

Nitrophenols constitute a class of volatile organic compounds that is increasingly present in urban as well as in natural environments [Leuenberger et al., 1985], [Tremp et al., 1993], [Lüttke and Levsen, 1997]. These compounds are used as raw materials in the chemical, pharmaceutical, dyes and herbicides 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.

Solubility of nitrophenols is larger than solubility of e.g. nitrobenzene, allowing measurements also of the standard derivative properties (i.e. calorimetric, densimetric that are derivatives of the standard chemical potential). As weak acids, nitrophenols are suitable for measurements of the ionization constants and include two functional groups of interest – nitro- and phenolate- groups – for possible extension of the existing high-temperature group contribution methods [Censky et al., 2007].

The thermodynamic data required to calculate the distribution of nitrophenols in environmental models have been measured [Müller and Heal, 2001], [Harrison, 2002], but only at near-ambient conditions. Possible remediation technologies such as steam oxidation require the 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 been measured up to 300°C for all three isomers [Hnedkovsky and Cibulka, 2003], and ionization constants that have been measured up to 200°C for p-nitrophenol by UV-visible spectroscopy [Shin et al., 1997]. Accurate ionization constants for the isomers of nitrophenol are also particularly useful in spectroscopic studies, because these compounds are 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 temperature and pressure are also necessary for the analysis of experimental measurements on all other thermodynamic properties of dilute nitrophenol or nitrophenolate solutions, because the raw data need to be corrected for ionization or hydrolysis, respectively (e.g. [Inglese et al., 1996]).

2.3 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

$$A(\lambda) = (\epsilon_{npOH}(\lambda) b m_{npOH} + \epsilon_{npO^-}(\lambda) b m_{npO^-})\rho_{solution} \tag{1}$$

where $A(\lambda)$ is the absorbance at wavelength λ,$\rho_{solution}$ is the solution density, b is the path length of the cell and the terms m_{npOH}, $\epsilon_{npOH}(\lambda)$ and m_{npO^-}, $\epsilon_{npO^-}(\lambda)$ are molalities and molar absorptivities of the indicator in the acidic form and its conjugate base. The absorptivities for the acidic and basic species were determined independently by measuring the spectrum of nitrophenol in a hydrochloric acid solution or that of nitrophenolate in a solution of ammonia or sodium hydroxide. Assuming no change in density of the solution with pH, Eq. 1 is transformed to

$$A(\lambda) = \frac{A_{acid}(\lambda)}{m_{acid}} m_{npOH} + \frac{A_{base}(\lambda)}{m_{base}} m_{npO^-} \tag{2}$$

where $\mathrm{X}_{\mathrm{acid}}$ and $\mathrm{X}_{\mathrm{base}}$ represent nitrophenol and nitrophenolate properties in the acidic and basic solutions, respectively.

For a given experimental spectrum, Eq. 2 includes two parameters ($\mathrm{m}_{\mathrm{npOH}}$ and $\mathrm{m}_{\mathrm{npO^-}}$) that can be determined by a least-squares regression.

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.

2. The ionic strength, activity coefficients and $K_{a,npOH}$ were calculated.

3. The system of mass action equations for ammonia, water and nitrophenol ionization 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 stabilized results.

2.4 Results

Typical spectra from one set of measurements on p-nitrophenol at 150 °C and pressure of 7 MPa is shown in Figure 1.

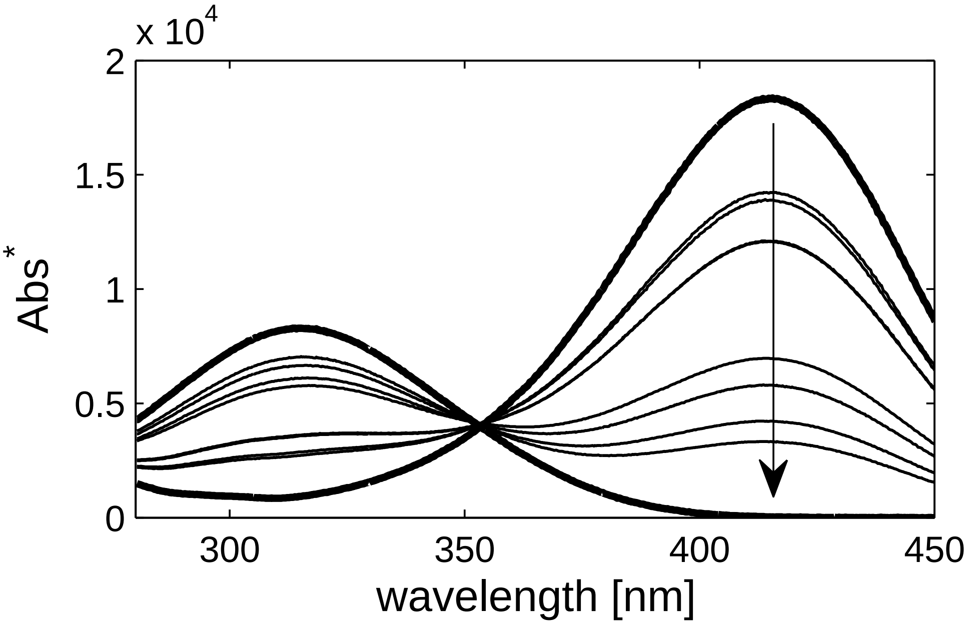

Figure 1: Spectra of p-nitrophenol at t = 200 °C , p = 7 MPa. Abs* is absorbance normalized by molality of the indicator. Bold lines correspond to acid and base extremes, the other lines are spectra of buffer solutions, the arrow indicates the direction of increase of pH.

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, which is consistent with the model presented above.

Literature values for the ionization constant of ammonia were obtained from the correlation of [Hitch and Mesmer, 1976]. The equilibrium constant for water was obtained from the new international formulation [Bandura and

Lvov, 2006] and activity coefficient products for water and nitrophenol ionization were assumed to be equal to the value of activity coefficient product in ammonia ionization, which was taken from [Hitch and Mesmer, 1976].

Table 1: Experimental values for $\mathrm{pK_a}$ of nitrophenols as a function of temperature at p = 7 MPa.

	o-nitrophenol	m-nitrophenol	p-nitrophenol
$t/°C$	pK_a	pK_a	pK_a
50	–	8.10±0.02[1]	–
100	6.73±0.04	7.77±0.03	6.58±0.06
150	6.64±0.04	7.63±0.02	6.45±0.05
175	6.66±0.05	7.62±0.03	6.39±0.06
200	6.70±0.03	7.60±0.03	6.44±0.03
225	6.80±0.03	7.61±0.04	6.53±0.02

2.5 Thermodynamic Model

Measured ionization constants can be combined with other data on nitrophenols ionization taken from literature ($\mathrm{pK_a}$ at 25°C , other data for derivatives of the ionization constant – enthalpy, volume, heat capacity). The integrated data can be used then for development of a complex thermodynamic model for ionization properties of aqueous introphenols.

As a thermodynamic model suitable for this purpose we have selected a model proposed originally by Marshall and Franck [Marshall and Franck, 1981] for the ionization constant of water, and worked on further by Mesmer et al. [Mesmer et al., 1988], [Anderson et al., 1991]. For $\mathrm{K_a}$ the expression is

$$\begin{aligned} \ln K_a = -pK_a \cdot \ln 10 = -\Delta G_a^o/(RT) = \\ a + b/T + c/T^2 + d/T^3 + (e + f/T + g/T^2) \cdot \ln \rho_w \end{aligned} \tag{3}$$

where G_a^o is the standard partial molar Gibbs energy of ionization; $a - g$ are model parameters; ρ_w is the specific density of water solvent. Other standard partial molar properties of ionization are obtained by appropriate derivations.

The experimental values of $\mathrm{pK_a}$ for the ionization of each nitrophenol isomer in Table 1 and the low temperature literature values were subjected to

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[1] Experimental uncertainty is calculated as a sum of standard deviation of experimental $\mathrm{pK_a}$s and a difference of average $\mathrm{pK_a}$ obtained from fitting the spectra, Eq. 2 , with and without the constraint of mass balance of total nitrophenol.

a simultaneous weighted fit. Parameters that were not statistically significant were removed from the fit, leaving typically four adjustable constants for each isomer in Eq. 3.

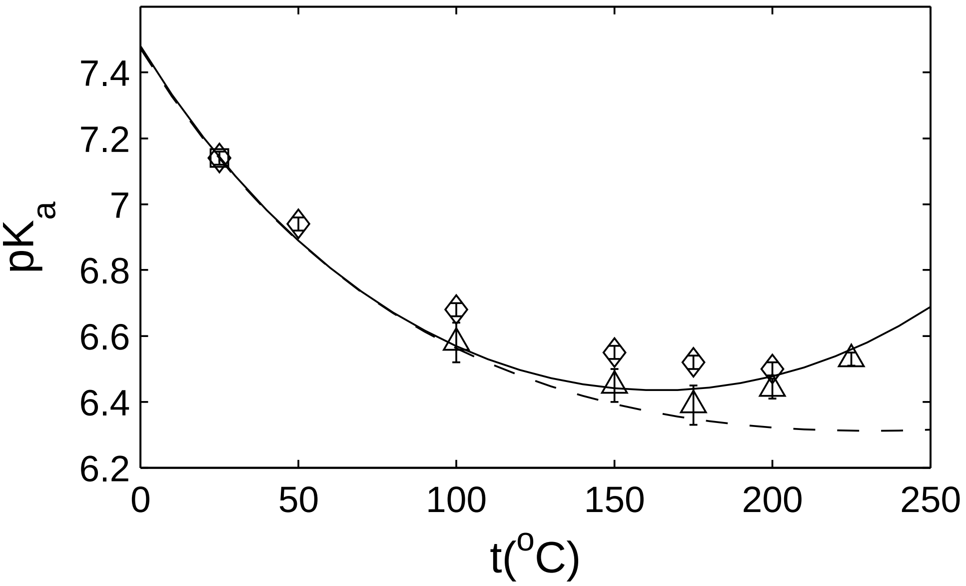

Figure 2: Ionization constant (pK_a) of p-nitrophenol as a function of temperature at p_{sat}. Predictions of Marshall and Franck model (full line); predictions from a van't Hoff thermodynamic integration (dashed line). Experimental data: [Judson and Kilpatrick, 1949] (square); [Shin et al., 1997] (diamonds); this work, corrected from p = 7 MPa to p_{sat} (triangles).

The effects of temperature and pressure on solvation are reflected in the standard state thermodynamic properties derived from the model. The calculated values for the standard Gibbs energy of ionization, $G_a{}^o$, are plotted in Figure 3.

There are significant differences in the properties of the three isomers. These can be most likely attributed to the electron-withdrawing effect of the nitro- group, which stabilizes the nitrophenolate anion and is larger for the o- and p- isomers than for m-nitrophenol (see, for example, [Dewick, 2006]). Intra-molecular hydrogen bonding of the phenolic group in o-nitrophenol may also be a factor.

2.6 Conclusions

Measured high-temperature ionization constants of aqueous nitrophenols were combined with other standard state properties on ionization reactions re-

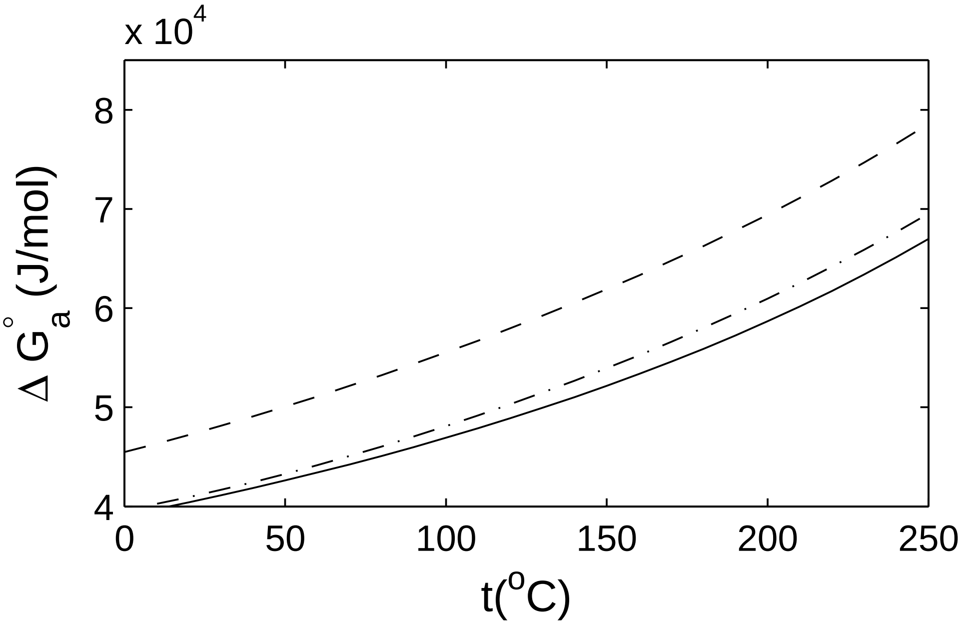

Figure 3: Standard partial molar Gibbs energy of ionization as a function of temperature at p_{sat}. Full line: p-nitrophenol; dashed line: m-nitrophenol; dash-dot line: o-nitrophenol.

trieved from the literature. The database was used for parameterization of the thermodynamic model, Eq. 3, describing the evolution of pK_a and other ionization functions with temperature and pressure. Applying Eq. 3 and its derivatives 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 instead the more complex model such as Eq. 3.

3 Copper-chloride complexation

3.1 Objectives

The aim of this study was to determine equilibrium constants and speciation of aqueous copper(II)-chloride complexes over a range of temperatures relevant for possible process optimization of the electrolysis step in the copper-chloride thermochemical cycle for hydrogen production. Following steps were pursued:

(i) Spectroscopic measurements at high temperatures and at elevated pressure for copper-chloride aqueous mixtures using UV-visible flow system.

(ii) Estimation of the number of absorbing factors, i.e. contributing aqueous complexes, using Principal Component Analysis.

(iii) Application of a suitable thermodynamic model for evaluation of copper-chloride complex formation constants.

The presented measurements are part of a broader project involving the study of complexation reactions in concentrated HCl solutions up to 13 mol/kg, and Cu(II) concentrations up to the solubility limit. Mononuclear copper complexes formed in dilute copper solutions as used in our work need to be thermodynamically determined prior to the intended measurements in copper-concentrated solutions that are actually applied in the technology for hydrogen production.

3.2 Previous studies

[Fritz and Königsberger, 1996] have compiled solubility data for cuprous and cupric chloride, CuCl and $CuCl_2$, in several chloride media including concentrated hydrochloric acid solutions. Unfortunately, there is only one set of data in this compilation that reaches 100°C , and the uncertainty is larger than that for data at lower temperatures. Most of the solubility studies at high temperature were intended to understand the transport and deposition of copper in ore-forming systems or concentrated brines [Crerar and Barnes, 1976] , [Fontana et al., 1983], [Xiao et al., 1998], [Liu et al., 2001], [Liu et al., 2002] and references herein). As a consequence, hydrochloric acid is only present at very low concentrations to avoid the hydrolysis of copper and the formation of hydroxyl-copper species. Stepwise formation constants for chloride with copper(I) and copper(II) have been reported by [Liu et al., 2002] and [Brugger et al., 2001].

In case of $CuCl_2$, extensive work has been done in the field of hydrometallurgy, mainly in concentrated $CuCl_2$-NaCl solutions at moderate temperatures [Berger and Winand, 1984], [Hyvärinen and Hämäläinen, 2005], [Lundström et al., 2005] . Much less has been done on the electrodeposition of copper from $CuCl_2$-HCl solutions, due to the difficulties associated with the use of concentrated HCl solutions [Kekesi and Isshiki, 1997]. The complexation of copper(II) with chloride was studied by [Brugger et al., 2001] in LiCl solutions up to 90°C and, according to the authors, there is evidence for the formation of up to four copper complexes. There are no accurate data for polynuclear copper complexes above 25°C .

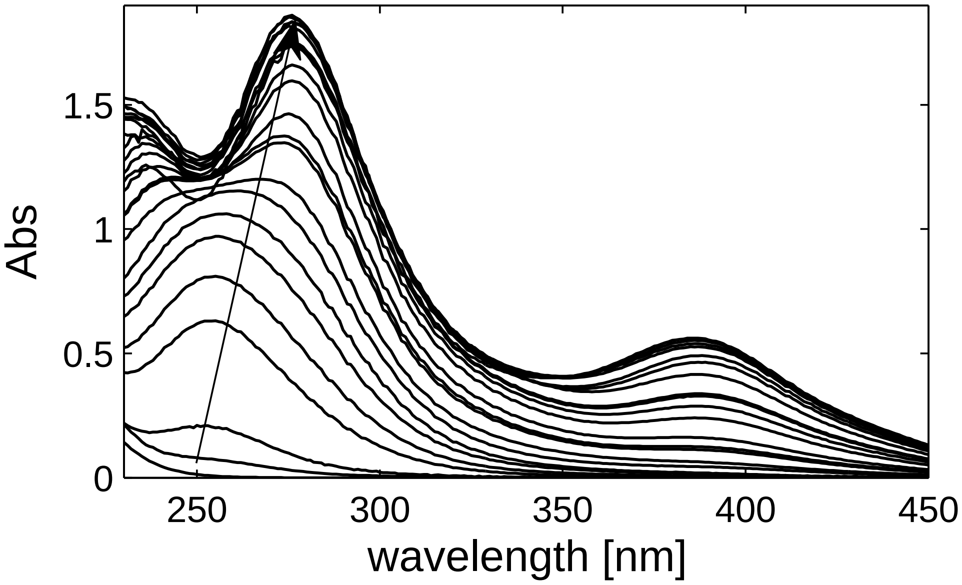

Figure 4: Baseline-corrected absorbance data of $[\mathrm{CuCl_n(H_2O)_{6-n}}]^{2-\mathrm{n}}$ in acidic LiCl solutions at 100°C and 9 MPa. Arrow indicates increasing chloride concentrations.

3.3 Analysis of the Spectroscopic Data

According to the Beer's law, the absorbance of a solution containing multiple absorbing species can be written as

$$A(\lambda) = \sum \epsilon_i(\lambda) b c_i \tag{4}$$

where $A(\lambda)$ and c_i are the molar absorptivity and molar concentration of species i, respectively, and b is the optical path length. For convenience, it was chosen to adopt a different concentration scale using units of mol per kg of solvent, rather than the usual molarity scale. To account for this transformation, a correction factor, f(ρ), had to be introduced in Eq. 4.

$$A(\lambda)/f(\rho_i) = \sum \epsilon_i(\lambda) b m_i \tag{5}$$

with

$$f(\rho_i) = \frac{1000\rho_{LiCl}}{1000 + m_{LiCl}M_{LiCl}} \tag{6}$$

where ρ_{LiCl} (kg/dm^3) is the density of LiCl solution at the same temperature, and $\mathrm{m_{LiCl}}$ (mol/kg) is the molality of LiCl in the copper solutions. The density of the LiCl solutions was calculated from the correlation by [Abdulagatov and Azizov, 2006]. The effect of solutes other than LiCl on the density of our solutions is neglected in Eq. 6, which is an acceptable approximation for our LiCl-dominated systems.

3.4 Results and Discussion

The baseline-corrected absorbance data such as those shown for 100°C in Fig. 4, were used for qualitative as well as quantitative analysis of complex formation in the copper-chloride systems. In addition to the complexation reactions, other reactions can take place, such as the formation of neutral ion pairs, $\mathrm{HCl^o}$ and $\mathrm{LiCl^o}$, at the concentration and temperature ranges covered in this study. The formation of polynuclear copper complexes was not considered in the data treatment since the concentration of copper is typically several orders of magnitude lower than that of the chloride:

$$[Cu(H_2O)_6]^{2+} + nCl^-(aq) \longleftrightarrow [CuCl_n(H_2O)_{2-n}]^{2-n} + nH_2O; \quad n = 1-4 \tag{7}$$

3.5 Qualitative Analysis

The first estimate of the number of absorbing aqueous species required to describe the experimental absorbance data was carried out using Principal Component Analysis (PCA). At experimental temperatures, PCA suggested that 5 factors are the minimum number required to be comparable with our experimental uncertainty. As a result, it was decided to include the formation of 4 mononuclear complexes up to $\mathrm{[CuCl_4(H_2O)_2]^{2-}}$, in addition to $\mathrm{[Cu(H_2O)_6]^{2+}}$. A solution of Beer's law, Eq. 5, was then obtained using the "model-free" approach described e.g. by [Brugger et al., 2001] with the constraints of positive molar absorptivity coefficients and concentrations, unimodality of the calculated concentration profiles of absorbing species, and fixed mass balance for copper-containing solutes. All calculations were performed with the software package BeerOz ([Brugger, 2007]). The results of this “model-free” regression can be used mainly for preliminary estimation of the relative abundance of absorbing species and confirmation of the proposed number of factors contributing to absorption. At all temperatures the distribution of species obtained from “model-free” fit is consistent with our assumption of 5 absorbing factors.

3.6 Thermodynamic Model

In addition to constraints applied in the “model-free” regression to Beer’s law, the concentrations of species present in any solution must obey the mass action laws for association reactions (LiCl, HCl) and complex formation reactions, as well as the mass balance equations for total Cu, Cl and Li. Simultaneous treatment of absorption data with all these equations and with a model for the activity coefficients allowed us to derive concentration profiles of absorbing species and their formation constants. Below are stated comments on the required input for the thermodynamic model, which includes association constants of HCl and LiCl and an assumption for activity coefficients of all species, ionic and neutral, in the solutions.

As a strong electrolyte, LiCl undergoes dissociation in aqueous solutions, which is almost complete at temperatures below 200°C and at low and moderate solute concentrations. As the temperatures or concentrations of the salt increase, ionic association becomes non-negligible and should be accounted for when modeling the thermodynamic behavior of such solutions. The association constants of LiCl were calculated from the Helgeson-Kirkham-Flowers (“HKF”) equation-of-state [Tanger and Helgeson, 1988] using parameters of the HKF equation for the ions from [Shock et al., 1997] and for the $LiCl^o$,aq ion pair from [Sverjensky et al., 1997]. The HKF model is semiempirical equation-of-state most widely used in geochemistry for calculation of thermodynamic properties at high temperatures and pressures.

Mean stochiometric activity coefficients for LiCl based on the ion-interaction approach, e.g. [Pitzer, 2000], were obtained from simultaneous correlation of isopiestic, phase equilibrium, electrochemical and calorimetric data to 250°C and ∼6 mol/kg by [Holmes and Mesmer, 1983]. If ion pairing is accounted for, these stochiometric activity coefficients need to be converted to the individual activity coefficients of the ions and the ion pair. The method that we chose for this purpose is described in detail e.g. by [Pokrovskii and Helgeson, 1997]. Since LiCl is always a dominant electrolyte in our solutions, we assumed that activity coefficients of all our ionic species are the same as for the Li^+ and Cl^- ions, in the case of H^+ and divalent ions the values differ by a constant in the activity coefficient model. The applied model for activity coefficients of the ions is given by

$$\log \gamma_i = -\frac{A|Z_K Z_A| I^{1/2}}{1 + a^0 B I^{1/2}} + \Gamma + b_i I + b_{i,sq} I^2 \tag{8}$$

where A and B represent the Debye-Hückel solvent parameters, a^0 denotes the distance of closest approach in a given salt, Z_K and Z_A are the charges of the cation and anion, respectively, $\Gamma = -\log(1 + 0.018053 m^*)$ designates the mole fraction to molality conversion, m^* is the sum of molalities of all solute species, $I = 1/2 \sum_{i=i}^{n} m_i Z_i^2$ is the molal-scale ionic strength, b_i represents the extended term for the electrolyte, which is a function of temperature and pressure, and $b_{i,sq}$ term is a further extension of the model used by [Pokrovskii and Helgeson, 1997] for application at molalities over ∼ 10 mol/kg.

For neutral ion pair $LiCl^0$ the activity coefficient was obtained from

$$\log \gamma_n = \Gamma + b_n I \tag{9}$$

where b_n is usually referred to as the Setchénow coefficient. The relation between the stochiometric and individual ionic activity coefficients is given by

$$\log \gamma^{st} = (1 - \alpha)\gamma_i \tag{10}$$

where α is the degree of association of the electrolyte, calculated from the mass action law.

The values of b_i, $b_{i,sq}$ and b_n for $LiCl^0$ were obtained by iterative process from the stochiometric activity coefficients from [Holmes and Mesmer, 1983]. Activity coefficients for neutral molecule $[CuCl_2(H_2O)_4]$ are unknown and were set accordingly to [Brugger et al., 2001].

3.7 Thermodynamics of Complex Formation

Regressions with a full thermodynamic model were also performed with the BeerOz software package [Brugger, 2007]. Following qualitative analysis by PCA, it was postulated that the model with 5 absorbing species at all temperatures is the most appropriate for data description. The calculated concentration profiles were physically realistic and relatively insensitive to changes in the database used for the fitting, for example, similar results were obtained after excluding absorbance data at wavelengths below 250 nm and/or excluding the absorbance data at concentrations above 10 mol/kg or even 6 mol/kg of Cl_{tot}. The same applies for the numerical stability of the calculated equilibrium constants of complexation reactions (Eq. 7), although the results at 150°C and especially 200°C were more sensitive to changes in the fitting database due to lower number of available spectra and Cl_{tot} concentration range.

Table 2: Values of logK at pressure of 9 MPa (formation constants for copper complexes, Eq. 7) derived from absorbance data.

t [°C]	$[CuCl]^+$	$[CuCl_2]$	$[CuCl_3]^-$	$[CuCl_4]^{2-}$
100	0.74	0.47	-0.84	-4.60
	(-0.3/+0.1)[2]	(-0.1+0.1)	(-0.1/+0.1)	(-0.1/+0.1)
150	1.04	1.46	-0.16	-1.94
	(-0.3/+0.3)	(-0.2/+0.4)	(-0.6/+0.1)	(-0.6/+0.7)
200	2.18	2.79	3.19	2.02
	(-0.3/+0.3)	(-0.8/+0.5)	(-2.4/+0.1)	(-2.0/+0.1)

Our results at 100°C are in good agreement with the values reported by [Brugger et al., 2001] at 90°C . The difference is negligible in case of $[CuCl(H_2O)_5]^+$, small and in trend with the lower temperature results in case of $[CuCl_2(H_2O)_4]$ and $[CuCl_3(H_2O)_3]^-$; the only difference outside the trend was found for the $[CuCl_4(H_2O)_2]^{2-}$ complex. However, uncertainty limits for $[CuCl_4(H_2O)_2]^{2-}$ formation constant are still larger than the observed disagreement between [Brugger et al., 2001] and this work results at 90°C , resp. 100°C .

Increasing trends for the dependency of formation constants with temperature are confirmed by this work. The predictions based of the HKF equation-of-state with parameters for copper complexes from [Sverjensky et al., 1997] compare quite favorably with the reported data, although the model parameters for complexes were obtained only from older experimental results at 25°C , using various empirical inter-correlations among these values and the HKF equation parameters. In case of $[CuCl(H_2O)_5]^+$ the predictions of the HKF model are semi-quantitative, for the higher complexes the agreement is qualitative.

3.8 Conclusions

UV-Vis absorption spectra were measured in acidic copper-chloride solutions at 100°C , 150°C and 200°C , 9 MPa, using a constant low concentration of

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[2] Experimental uncertainty is estimated from maximum and minimum differences obtained by regression with database subsets.

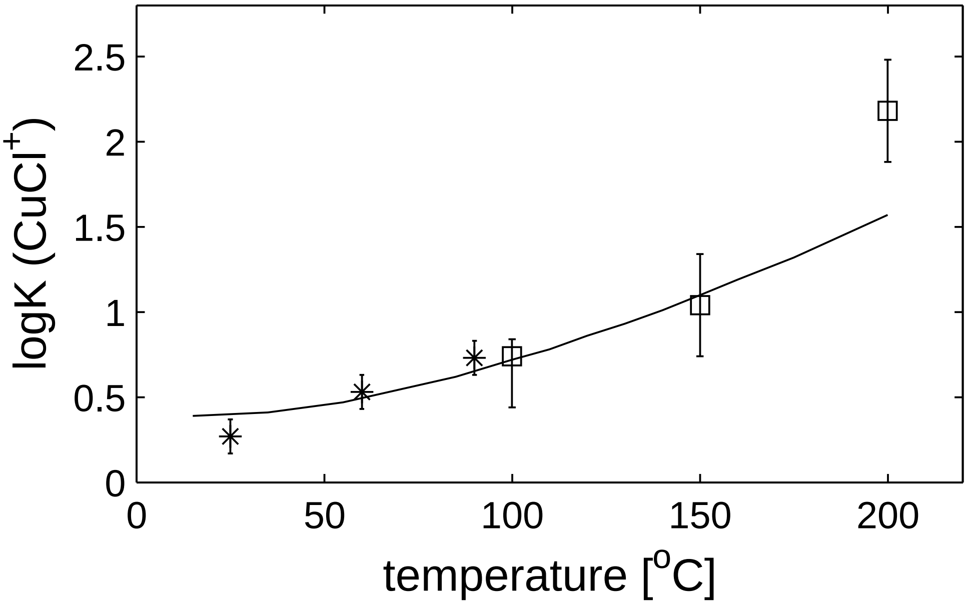

Figure 5: Formation constants for copper complex $[CuCl(H_2O)_5]^+$, logK, as a function of temperature. Stars: [Brugger et al., 2001], squares: this work. Line: HKF predicted values at 9 MPa.

Cu and Cl_{tot} concentration up to 17 mol/kg. Thermodynamic formation constants of the copper-chloride complexes were retrieved from the experimental data using appropriate physical-chemical constraints. The results reported in this work are in good agreement with data and trends from the previous studies. A plan for extending the measurements and alternative modeling of activity coefficients has been developed, in order to obtain reliable thermodynamic representation of copper-chloride complexation to at least 473 K suitable for parameterizing engineering models for the copper-chloride thermochemical hydrogen production cycle (aqueous part). We consider these efforts a necessary step towards developing a model for even more complicated mixtures of copper-chloride complexes, including polynuclear ones, that resemble the systems proposed for the copper-chloride cycles evaluated for hydrogen production.

4 Summary and Conclusions

High-temperature, high-pressure UV-visible spectrometry in flow arrangement has been used in this work to study thermodynamic properties of selected aqueous systems.

The first section was devoted to thermodynamic properties of all three isomers of aqueous nitrophenols. Ionization constants up to 225°C were measured in the experimental part that were then combined with the other standard state properties of ionization reactions from the literature and thermodynamic model was developed to describe thermodynamic properties of ionization for aqueous nitrophenols as a function of temperature and pressure. The results have several direct applications e.g. in environmental modeling (air-water distribution of nitrophenols and their reactions in water droplets), in spectrophotometry (nitrophenols can be used as high-temperature pH indicators) and in interpretation of other experimental measurements for these systems (corrections for ionization of calorimetric or densimetric results). Another purpose of our study was to obtain reliable high-temperature data that would allow, along with other experimental results retrieved from the literature, extension and/or verification of the existing high-temperature group contribution methods by nitro- and phenolate- functional groups.

The second part of the thesis included measurements of copper-chloride complexation in aqueous solutions at temperatures 100°C , 150°C and 200°C at a constant low concentration of copper and at different concentrations of chlorides. Principal Component Analysis and the extended model for activity coefficients of aqueous species were used to elucidate the formation constants of the mononuclear Cu(II)-chloride complexes. Five absorbing species were found necessary to describe the measured absorptivities within the limits of the analytical uncertainty. In addition to $[Cu(H_2O)_6]^{2+}$, formation constants were evaluated for four copper-chloride complexes: $[CuCl(H_2O)_5]^+$, $[CuCl_2(H_2O)_4]$, $[CuCl_3(H_2O)_3]^-$ and $[CuCl_4(H_2O)_2]^{2-}$. The results are considered as a part of a larger project leading to thermodynamic model of concentrated copper-chloride systems in a wide range of conditions that could be applied in technology optimization of the copper-chloride thermochemical cycle for hydrogen co-generation from the SCWR cycle.

Two different systems that were studied required a rather broad thermodynamic background for appropriate data interpretation. Nonetheless, UV-visible flow spectroscopy at high temperatures and pressures proved to be a valuable technique to complement the other common experimental approaches in high-temperature solution chemistry and we plan to explore this method also in the future.

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List of related publications

Journal papers

- Ehlerova, J., Trevani, L.N., Sedlbauer, J. and Tremaine, P.R.: Spectrophotometric Determination of the Ionization Constants of Aqueous Nitrophenols at Temperatures up to 225°C . J Sol. Chem., 37(6), 857–874 (2008)

- Trevani, L.N., Ehlerova, J., Sedlbauer, J., Tremaine, P.R.: Complexation in the Cu(II)-LiCl-H_2O System at Temperatures to 423 K by UV-Visible Spectroscopy, Int. J. Hydrogen Energy (submitted)

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- Ehlerova, J., Trevani, L.N., Sedlbauer, J. and Tremaine, P.R.: Ionization constants of aqueous nitrophenols at temperatures to 225°C using UV-visible spectroscopy. IAPWS meeting, Luzern, Switzerland, August 26–31, 2007

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- Trevani, L.N., Ehlerova, J., Sedlbauer, J. and Tremaine, P.R.: Complexation in the Cu(II)-LiCl-H_2O System at Temperatures to 150°C by UV-Vis Spectroscopy. International Conference on Hydrogen Production, University of Ontario Institute of Technology, Oshawa, Ontario, Canada, May 3–6, 2009 (fulltext)

- Ehlerova, J., Trevani, L.N., Sedlbauer, J. and Tremaine, P.R.: Complexation in the Cu(II)-LiCl-H_2O System at Temperatures to 200°C by UV-Vis Spectroscopy. IAPWS meeting, Doorwerth, Netherlands, September 6–11, 2009