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SUB- AND SUPERCritical WATER

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MASS TRANSFER IN SCWO PROCESSES: MOLECULAR DIFFUSION AND
MASS TRANSFER COEFFICIENTS OF INORGANIC NITRATE SPECIES IN
SUB- AND SUPERCRITICAL WATER

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Abstract

Molecular diffusion coefficients of lithium-, sodium-, potassium-, cesium-, calcium-, and strontium nitrate in subcritical water were determined by analysis of Taylor dispersion profiles. Pressures ranged from 300 to 500 bar at temperatures ranging from 25°C to 300°C. The reported diffusion values were determined at infinite dilution. Molecular diffusion coefficients were 10 to 20 times faster in near-critical subcritical water than in water at ambient temperature and pressure (ATP). These findings implied that the diffusion rates were more liquid like than they were gas like, hence experimental results were correlated with diffusion models for liquids. The subcritical diffusion data presented in this work, and supercritical diffusion results published elsewhere were correlated with hydrodynamic diffusion equations. Both the Wilke-Chang correlation and the Stokes-Einstein equation yielded predictions within 10% of the experimental results if the structure of the diffusing species could be estimated. The effect of the increased diffusion rates on mass transfer rates in supercritical water oxidation applications was quantified, with emphasis on heterogeneous oxidation processes. This study and results published elsewhere showed that diffusion limited conditions are much more likely to be encountered in SCWO processes than commonly acknowledged.

Introduction

Inorganic nitrate and nitrite species - with or without a co-oxidant - can successfully be used for oxidation of ammonia and organic pollutants in a supercritical water oxidation (SCWO) process. This is particularly interesting for the many waste streams that contain significant levels of nitrogen containing species. Although many studies have been documented in the literature about the chemistry and kinetics of nitrate and organic destruction, physical transport phenomena in water at elevated temperatures and pressures - and their impact on homogeneous and heterogeneous reactions, corrosion, heat exchange, (reactive) extraction, filtration - are not adequately understood. This situation is largely due to the limited data that is available for diffusion in high

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temperature, high pressure water mixtures. Only the molecular diffusion of iodide-ions and hydroquinone in near-critical subcritical water and the self diffusion coefficient of compressed sub- and supercritical water have been reported. These results indicate that diffusion in supercritical and near-critical subcritical water is about 15-35 times faster than in water at ambient temperature and pressure (ATP).

The purpose of this study was: (1) to determine the molecular interdiffusion of inorganic nitrate species in sub- and supercritical water, and (2) to evaluate the potential effects of diffusion limited conditions in heterogeneous oxidation processes at elevated temperature and pressure. Molecular diffusion coefficients of lithium-, sodium-, potassium-, cesium-, calcium-, and strontium nitrate in subcritical water were determined by analysis of Taylor dispersion profiles. Pressures ranged from 300 to 500 bar at temperatures ranging from 25°C to 300 °C resulting in water densities ranging from about 1.0 to 0.70 g/cc. The reported diffusion values were determined at infinite dilution. In addition, diffusion results for sodium nitrate in concentrated hydrothermal solutions (400 < T < 500°C; 250 < P < 1000 Bar; 0.25 < c < 3.0 m) were determined by the laser induced grating technique and are discussed elsewhere. The temperature and pressure conditions selected are of interest for Wet Air Oxidation and Supercritical Water Oxidation. Experimental diffusion results were correlated with predictions from theoretical diffusion models.

**Experimental Technique**

The Taylor dispersion technique is based on the diffusion equation for laminar flow solved for a Dirac-δ pulse input. If a narrow pulse of soluble substance is injected in the laminar flowing fluid, the pulse spreads due to the combined action of convection and molecular diffusion in the axial direction and molecular diffusion in the radial direction. Taylor showed that the longitudinal dispersion of a tracer "relative to a plane which moves with velocity 1/2v₀" behaves "exactly as though it were being diffused by a process which obeys the same law as molecular diffusion but with a diffusion coefficient K", resulting in the dispersion equation (Eq. 1):

\[
\frac{\partial C}{\partial t} = K \frac{\partial^2 C}{\partial x^2} \tag{1}
\]

with,

\[
K = D_{12} + \frac{v_{av}^2 a^2}{48D_{12}} \tag{2}
\]

where \( x' = x - 1/2v_0t \) and \( v_{av} \) is the average fluid velocity. The solution by Taylor is subject to several constraints: (1) a perfect Dirac-δ input function, (2) laminar, incompressible flow of a Newtonian fluid, (3) axial molecular diffusion negligible compared to axial convective transport and the radial concentration gradient becomes negligible due to radial diffusion, (4) diffusion coefficient is independent of concentration, (5) constant fluid density throughout the diffusion tube, (6) no chemical reaction is occurring during the experiment, and (7) the dispersed pulse is symmetrical in shape. Details are provided in Levelt-Sengers and co-workers and Erkey and Akgeman. For relatively large values of ε, the condition to validate whether axial diffusion and the radial concentration gradient are negligible is given by Eq. 3:

\[
\frac{1}{13.8} \gg \frac{D_{12}}{2v_{ava}} = \varepsilon \gg \frac{a}{8L} \tag{3}
\]
For a Dirac-$\delta$ pulse input of mass $M$, the solution for Eq. 1 - the radially averaged concentration $C$ at the end of the diffusion tube - is given by Eq. 4:\textsuperscript{12,13}

$$C = \frac{M}{\pi a^2 \sqrt{4\pi Kt}} \exp \left( \frac{-(L-v_gt)^2}{4Kt} \right)$$ \hspace{1cm} (4)

The experimental dispersion profile was fitted to Eq. 4 using the parameter estimation method.\textsuperscript{12} In this method, the detector output (voltage) is used directly to calculate the diffusion coefficient. The mathematical model for the voltage output representing Eq. 4 is presented by Eq. 5:

$$V = \frac{m_1}{\sqrt{t}} \exp \left[ -\frac{(L-m_3t)^2}{m_2t} \right] + m_4 + m_5$$ \hspace{1cm} (5)

where $m_1$ equals $M/\pi a^2 \sqrt{4\pi K}$, $m_2$ equals four times the dispersion coefficient, $m_3$ is the average solvent velocity, and $m_4$ and $m_5$ account for baseline offset and drift. Eq. 5 was fitted to the experimental data using non-linear least-squares analysis, by means of the Marquardt-Levenberg algorithm. Initial estimates for $m_4$ and $m_5$ were obtained by linearly interpolating between the starting and end points of the dispersion peak signal. The average fluid velocity was used as an initial guess for $m_3$. Initial guesses for $m_2$ were obtained from the graphical method.\textsuperscript{12} The molecular diffusion coefficient was then calculated from Eq. 7:\textsuperscript{12}

$$D_{12} = \frac{m_2}{8} \sqrt{\frac{m_2^2}{64} - \frac{(am_3)^2}{48}}$$ \hspace{1cm} (6)

where $a$ is the diffusion tube radius ($a=1.163$ mm). Reported diffusion coefficients are the average of about six repetitions.

The laser-induced grating technique has been discussed in detail elsewhere.\textsuperscript{1} The laser-induced grating technique and Taylor dispersion technique are highly complementary because the former yield optimal results at high concentrations, and near the critical point,\textsuperscript{1} two conditions for which the Taylor dispersion method becomes increasingly more difficult.\textsuperscript{11}

**Experimental Apparatus**

The schematic diagram of the experimental apparatus used in this work is shown in Fig. 1. Fluid delivery and pressure control were provided by two syringe pumps with a capacity of 250 mL (ISCO Model LC-2600), with one pump providing the feed flow and the other receiving the effluent at the end of the tube. The diffusion tube was a 3.500 ±0.001 meter long, straight Inconel 625 tube (OD = 6.35 mm, ID = 2.33 mm). The effect of the thermal expansion was incorporated in the data analysis. Six well insulated brass heaters were installed along the entire length of the tube. Each heater was independently controlled by a temperature controller (Omega Model CN9000A). Two thermocouples were installed for each heater element, with the last one being used as input to the temperature controller. Thermocouples installed along the diffusion tube monitored the tube wall temperature which matched the fluid temperature to within 1°C. This experimental apparatus allowed for a temperature control better than ±2°C and pressure control better than ±2 Bar. At subcritical conditions this resulted in a density control better than ±1% which approximately satisfies the maximal allowable density gradient as discusses in Levelt Sengers and co-workers.\textsuperscript{11} In addition, the syringe pumps delivered pulse-free low speed flows...
with Reynolds numbers ranging between 5 and 60. The small fluid velocities and small temperature gradients ensured incompressible flow conditions.\textsuperscript{14}

A "Dirac-\(\delta\) input function" was obtained by using a HPLC injection valve rated for 480 Bar (Rheodyne Model 7000) at 80°C prior to a preheater. The total volume of the input function (an inorganic nitrate solution between 0.005 and 0.10 molal in concentration depending on the temperature) did not exceed 100 \(\mu\)L after expansion, or less than 1\% of the volume of the diffusion tube. As was shown by Evans and Kenney\textsuperscript{15} and Levenspiel and Smith,\textsuperscript{16} imperfections in the input can be neglected if the injected sample volume does not exceed 1\% of the volume of the dispersion tube.

UV-Vis absorption of nitrate was employed to detect the dispersion profile. An optical cell similar to the one described by Anderson\textsuperscript{17} was used in the UV diagnostics of the eluted dispersion profile. The optical cell was maintained at the same temperature and pressure as the diffusion tube. Temperature control was accomplished by four cartridge heaters (Omega 120V, 150W) inserted in a brass block surrounding the optical cell. The optical diagnostics for the eluted pulse consisted of a deuterium lamp (Oriel Model 6000), a narrow band optical filter (Oriel 53000 Series), a fused silica neutral density filter used as beamsplitter (Melles Griot, Model 03-FNQ-003), a fused silica focusing lens, two photomultiplier tubes (Hamamatsu Model R955) with high voltage power supplies (Power Designs, Inc., Model 2K20), two lock-in amplifiers (Ortec Model 9503), and a voltmeter (Tektronix Model DM502A). A schematic of the optical layout is shown in Fig. 2. The beam of the deuterium lamp was filtered for the desired wavelength and split into two beams. One beam was used as reference signal, the other passed through the focusing lens and optical cell. The signals of the two PMT's were amplified and ratioed by the lock-in amplifiers. The ratioed signal was displayed by the voltmeter.

Thirteen temperatures, two pressures, and the voltage from the UV absorbance assembly were monitored by a Stanford Research SR630 thermocouple monitor. The thermocouple monitor was interfaced with a Macintosh Quadra 650 computer using a LabVIEW\textsuperscript{®} program. All channels were recorded simultaneously at a rate of 0.1 Hz.

**Molecular Diffusion Models**

Four approaches can be used to model diffusion coefficients in the region where critical effect can be neglected: hydrodynamic, kinetic, activation, and free volume theories.\textsuperscript{18} Supercritical fluids are frequently correlated to some variant of hydrodynamic theory or kinetic theory. Although these two approaches inadequately describe the complex thermodynamic behavior of supercritical solute/solvent systems, they yield accurate predictions when the solute is dilute and strong compositional effects can be ignored.\textsuperscript{19} Diffusion results for organic molecules in non-aqueous supercritical solvents\textsuperscript{20} indicate that diffusion in supercritical and near-critical subcritical solvents are about ten times faster than in liquids at ATP, but about a thousand times slower than in gases. Hence, hydrodynamic theory - which is typically employed to describe diffusion in liquids - provides a simple framework for diffusion in sub- and supercritical fluids. For this work, experimental results were compared with simple hydrodynamic and electrochemical models.

In hydrodynamic theory, the diffusion coefficient is thought to be a function of the bulk solvent viscosity, temperature, and some function of the solute size. The Stokes-Einstein relation for rigid spherical particles regards the solute molecule as moving in a continuum solvent. "Slip" between the solvent and solute molecules is ignored. The Stokes-Einstein relation in the no-slip limit is given by:
\[ D_{12} = \frac{kT}{6\pi\mu(\sigma/2)} \]  

where \( T \) is the temperature in Kelvin, \( k \) the Boltzman constant, and \( \sigma \) the molecular diameter (for electrolytes the average ionic diameter). A more general equation would be to replace the denominator by a frictional coefficient. This frictional coefficient is generally a function of the solute geometry, solvent viscosity, and a coefficient to account for slip between solute and solvent\(^1\). Many hydrodynamic correlations have been developed, the most well known of which is the dimensional expression proposed by Wilke and Chang:\(^{21}\)

\[ D_{12} = 7.4 \times 10^{-15} (\beta M_2)^{0.5}(\nu_1)^{-0.6}T \mu^{-1} \]  

where \( D_{12} \) in m\(^2\)/s, \( T \) in Kelvin, \( \mu \) in Pa.s, the molar volume \( (\nu_1) \) in cm\(^3\)/mole, and \( M_2 \) the molecular mass in g/mole. \( \beta \) is an empirical constant that corrects for solvent self-association.

For infinitely dilute electrolytes, the Nernst-Einstein equation is the basis for correlation expressions. The Nernst-Einstein equation\(^{18}\) was formulated for ions in infinitely dilute electrolyte solutions where anions and cations exert no influence on each other (Eq. 9):

\[ D_{12} = \frac{|z_+| + |z_-|}{|z_+z_-|} \frac{RT}{F^2} \frac{l_+l_-}{l_+ + l_-} \]  

where \( l_+ \) and \( l_- \) are the limiting equivalent conductivities of the cations and anions respectively (cm\(^2\)Ω\(^{-1}\)mol\(^{-1}\)), \( R \) the universal gas constant (=8.316J/mol.K), \( z_+ \) and \( z_- \) the charge of the cation or anion respectively, and \( F \) the Faraday number (=96,500C/mol). Many correlations based on the Nernst equation exist.\(^{22}\)

Results and Discussion
The diffusion coefficients for the alkali nitrates are shown in Fig. 3, where the values at 25°C are literature values at 1 atm.\(^{23}\) The 95% confidence interval was typically ±10% around the mean. Diffusion coefficients increased about 15 fold over the temperature range 25-300°C. In addition, Fig. 3 shows that for the 25 to 300°C temperature range the diffusion coefficient decreases with decreasing cation radius as is observed at ATP. This observation is commonly explained by the increased size of the hydration sphere caused by the increased charge density for smaller ions. Similar behavior is observed for the alkali-earth nitrates as shown in Fig. 4. The results at 250 and 300°C are currently being verified. As was expected by evaluating liquid diffusion models and solvent compressibility data, the pressure effect is minimal at subcritical conditions (Fig. 5). Observed pressure effects in the diffusion coefficients for all studied alkali and alkali-earth nitrates were well within the experimental uncertainty. These diffusion results agree well with the diffusivities determined by Flarsheim and co-workers\(^3\) for iodide ions using chronoamperometry. Fig. 6 shows diffusion coefficient for sodium nitrate in a 1.0 m hydrothermal solution.\(^1\) The critical temperature at this concentration was estimated to be around 425°C,\(^{17,24}\) hence the 400°C data represents subcritical conditions. These results have been discussed in detail elsewhere,\(^1\) but the main conclusions are repeated: (1) at high-density sub- and supercritical conditions the diffusion coefficients reach a plateau value that is about 20-25 times larger than ATP diffusion values, (2) very near the phase-separation pressure the diffusion coefficients approach values less than their ATP values - the so called “critical slowing down” of the diffusion coefficient - and (3)
these critical effects are important as far as 200 bar from the phase-separation pressure, corresponding to solution densities less than about 0.475 g/cc.

Correlation of the sub- and supercritical diffusion results with Eq. 7, 8, and 9 is incomplete at this point. Fig. 5 shows the correlation between the Stokes-Einstein equation - with the average ionic radius calculated from published diffusion data at ATP and sodium nitrate diffusion data. Similar graphs were obtained for the other alkali nitrates, and the alkali-earth nitrates. Negative deviations from the Stokes-Einstein equation increase with increasing temperature up to about 200 °C. These deviations indicate an increase in average ionic radius with increasing temperature. This increase can be explained by an increase of the radius of the hydration sphere surrounding the ions and/or by an increase in the degree of ion association. At temperatures exceeding 200°C, the group D$_{\mu}/kT$ is essentially constant, where the constant value is given by $(6\pi\eta R_0)^{-1}$, with $R_0$ the radius of the diffusing species at ATP and $\eta$ a constant between 1.2 and 1.8 depending on the species. It was shown by Butenhoff and co-workers$^1$ that at densities exceeding 0.475 g/cc and temperatures exceeding the critical temperature, the experimental results correlated well with the Stokes-Einstein equation or Wilke-Chang correlation with the diffusing species represented as a hydrated contact ion-pair. These preliminary modeling results indicate that diffusion in sub- and supercritical water can be estimated by the Stokes-Einstein equation if the size of the diffusing species is known or can be estimated.

The Nernst-Einstein equation is only applicable at conditions where the diffusing species is dissociated: in subcritical water, and - to a lesser degree - high density supercritical water. Limiting electroconductivity values were obtained through a relative method and are currently being reduced. Progress will be documented in a forthcoming publication.

To illustrate the potential importance of accurate knowledge about mass diffusion in sub- and supercritical water, the oxidation of biomass by sodium nitrate was evaluated. This example was chosen in light of recent work performed at Los Alamos National Laboratory which illustrated the potential of treating two waste streams - one high in nitrate concentration the other containing organic contaminants - by combining them at hydrothermal conditions.$^2$ This work focused on homogeneous conditions and is described elsewhere in this volume, however many heterogeneous waste streams are present within the DOE complex that contain high concentrations of inorganic nitrates and/or organic compounds. Because of the fast chemical kinetics associated with SCWO (and WAO), diffusion limiting conditions are likely to be encountered in heterogeneous systems. For the sample calculations it was assumed that the heterogeneous oxidation of biomass (C$_5$H$_7$O$_2$N) by NaNO$_3$ could be described by the shrinking sphere model with fluid-film diffusion as the rate limiting step. This model provides a good first approximation of the oxidation of a coal particle in the gas phase.$^{25}$ The calculations were performed for a biomass particle of 1 mm radius, with a velocity around the particle of 1 mm/s, and a slight excess in nitrate for the redox reaction (C$_1$/C$_2$ = 7). For this scenario, the mass transfer coefficient (k) is given by Eq. 10:$^{26}$

$$k = 0.42 \frac{\sqrt{v} D_{l2}^{2/3} \rho^{1/6}}{\mu^{1/6} \sqrt{r}}$$

where $r$ is the radius of the biomass particle, and $v$ the velocity around the particle. The results are given in Fig. 7. In subcritical water (WAO) the time needed for the reaction to go to completion decreases with increasing temperature due to the increased diffusion coefficients. However, for conditions typically associated with the SCWO process critical effects become important. As a result, the reaction time increases with increasing temperature in the supercritical region due to the critical slowing down of the diffusion coefficient. At 450°C and 425 Bar, the reaction time would
be about twice as long as what would be expected if the diffusion coefficient were estimated using 
the Stokes-Einstein equation or Wilke Change correlation. These critical effects are expected to 
decrease with decreasing concentration.27

Conclusions
Molecular diffusion coefficients of electrolytes increase with increasing temperature to values at 
high-density supercritical and near-critical subcritical water that are about 10 to 20 times the values 
at ATP. However, the increase is not as significant as expected from hydrodynamic theory. This 
negative deviation is probably the result of the change in size of the diffusing species due to a 
change in the solvation environment and/or ion-association.

The critical slowing down of the diffusion coefficient is important as far as 200 Bar from the phase 
separation pressure and is expected to become less significant with decreasing concentration. 
Calculations for heterogeneous oxidation reactions illustrate the importance of accurate knowledge 
of the mass transport phenomena at WAO or SCWO process conditions.

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Fig. 1. Molecular Diffusion Apparatus with Straight Diffusion Tube
Fig. 2. UV-Vis Absorption Diagnostics for Detection of the Dispersion Profile

Fig. 3. Alkali-Nitrate Diffusion Coefficients at 300 Bar. The Values at 25°C Are at 1 Atm. The 95% Confidence Interval is Typically ±10% Around the Mean.
Fig. 4. Alkali Earth-Nitrate Diffusion Coefficients at 300 Bar (Error Bars are ± 2 Standard Deviations).

Fig. 5. Pressure Effects on the Diffusion Coefficient of NaNO₃ in Subcritical Water. The line is the Value Calculated from the Stokes-Einstein Equation and the Diffusion Coefficient at 25°C and 1 Atm² (Error Bars are ± 2 Standard Deviations).
Fig. 6. Diffusion Coefficients of NaNO₃ in 1.0 m Hydrothermal Solutions as a Function of Temperature and Pressure. Taken from Butenhoff et al.¹ (Error Bars are ±1 Standard Deviation).

Fig. 7. WAO and SCWO Oxidation of Biomass with NaNO₃ Assuming the Shrinking Sphere Model with Fluid Film Diffusion as the Rate Limiting Step. Note that the "Experimental Curves" were Obtained by Incorporating the Experimentally Obtained NaNO₃ Diffusion Coefficients in Eq. (10).
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