

Solution chemistry in supercritical water: spectroscopy and simulation Keith P. Johnston,
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Fundamental chemical properties of supercritical water solutions are discussed including ion solvation and acid-base equilibria, which play a central role in solvent effects on chemical reaction rate and equilibrium constants, phase equilibria, and corrosion. These properties are evaluated on the basis of in-situ spectroscopic measurement of chemical equilibria and computer simulation. The recent development of relatively stable organic UV-visible pH indicators for SCW offers the opportunity to measure equilibrium constants quantitatively, to characterize buffers and to monitor acid-base titrations. On the basis of molecular dynamics computer simulation, the behavior of thermodynamic properties for equilibrium reactions, including acid-base reactions, are analyzed in terms of solvation structure at a molecular level. Diffusion coefficients of ions are determined by computer simulation from water rotational orientation times about ions.

Acid-Base Behavior in Hydrothermal Processing of Wastes

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Understand and predict

- H-bonding
- ion solvation
- acid-base behavior
- solvation along a reaction coordinate
- diffusion

Tools

- spectroscopy
- computer simulation
- molecular thermodynamic models

Relevance

- phase behavior and salt solubility
- solvent effects on rate and equilibrium constants
- activities of catalysts
- corrosion

HYDROTHERMAL OXIDATION (above 374 C)

Advantages:

1. Lower emissions than incineration
 - homo. rxn- high solubilities of organics and O₂
 - conversions > 99.99% above 550 C in < 1 min.
 - gases: CO₂, H₂O, and N₂
 - heteroatoms precipitate as salts
 - small amount of particulates are trapped by water
2. Lower T than incineration
 - higher energy efficiency- can treat dilute streams
 - thermodynamics favors less NO_x
3. Versus wet-air oxidation:
 - short residence times
 - oxygen is miscible
4. Control chemistry by varying dielectric constant
5. Politically more acceptable than burning

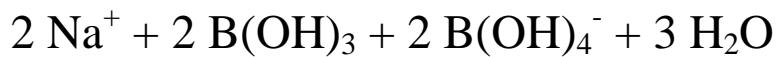
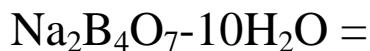
Disadvantages:

Corrosion, salt recovery, high P, new science and tech.

ACID-BASE TITRATIONS MONITORED WITH ORGANIC INDICATORS IN SCW



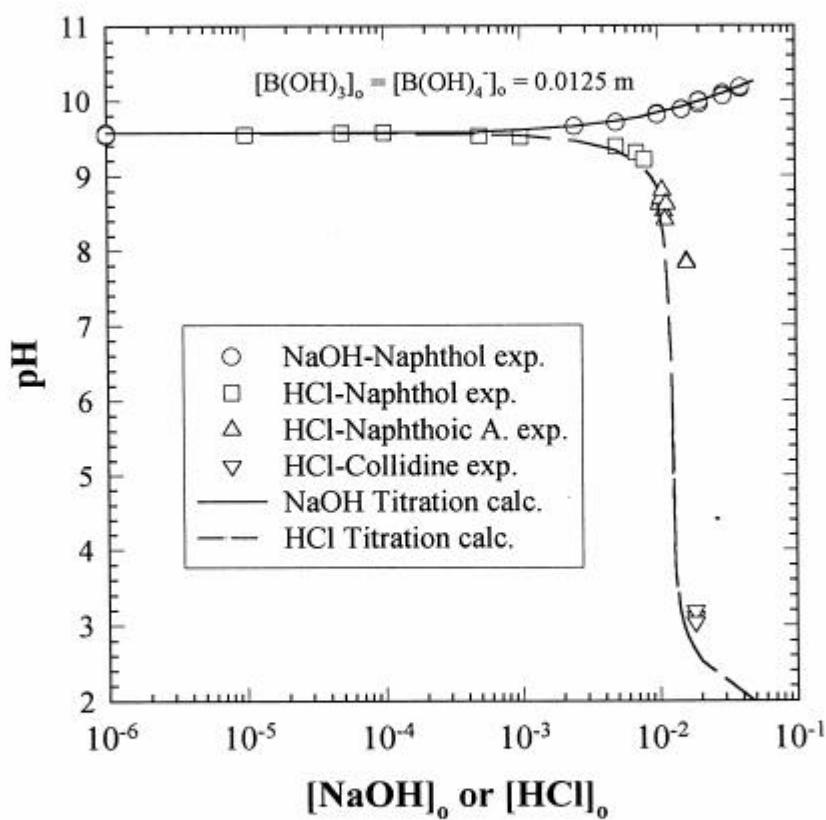
Borate buffer:



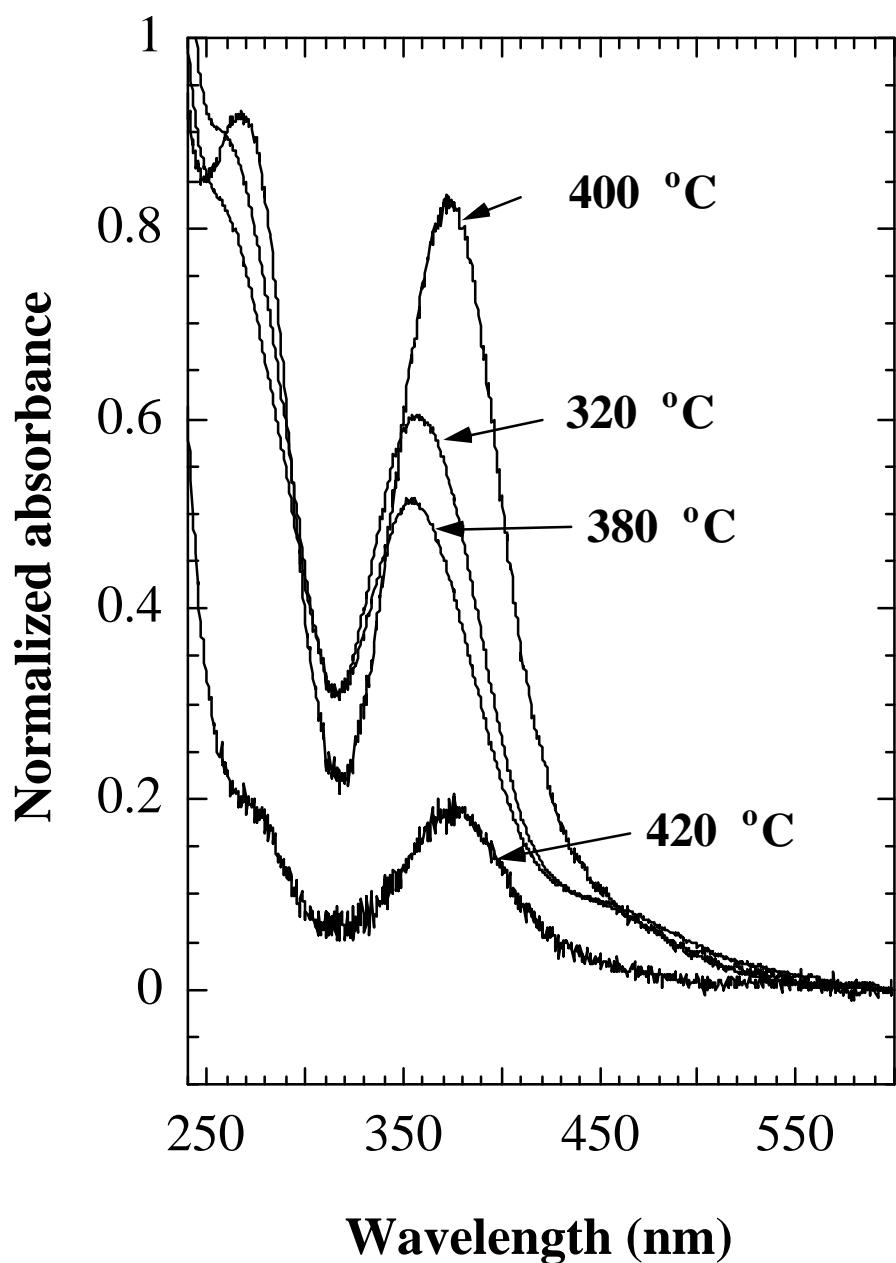
2-naphthol
2-NPCOOH
collidine

Buffer capacity vs. KOH, HCl

Titration of Sodium Borate with NaOH and HCl at 350°C, 3500 psia

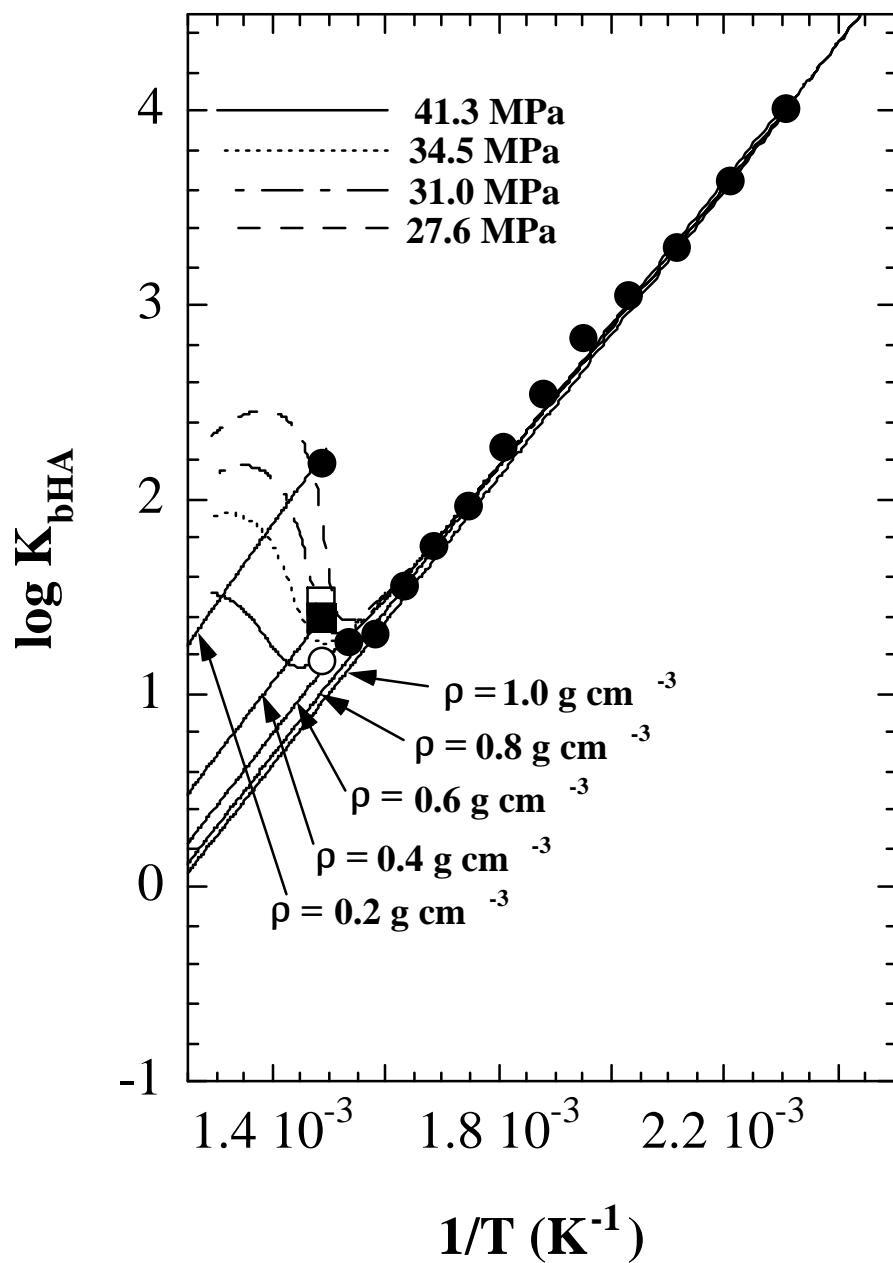


UV-vis spectra of 2.5×10^{-4} m $\text{K}_2\text{Cr}_2\text{O}_7$ in water with 2×10^{-3} m KOH at 27.6 MPa



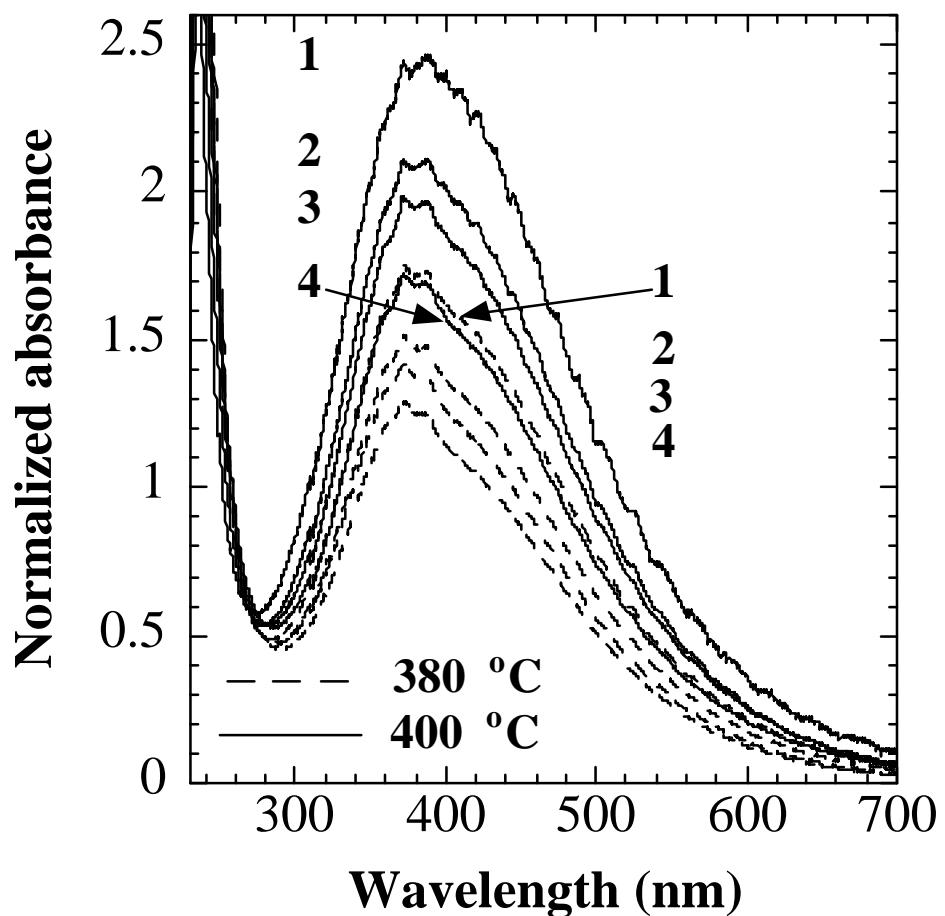
K_{bHA} for the reaction $HCrO_4^- + OH^- \Rightarrow CrO_4^{2-} + H_2O$.

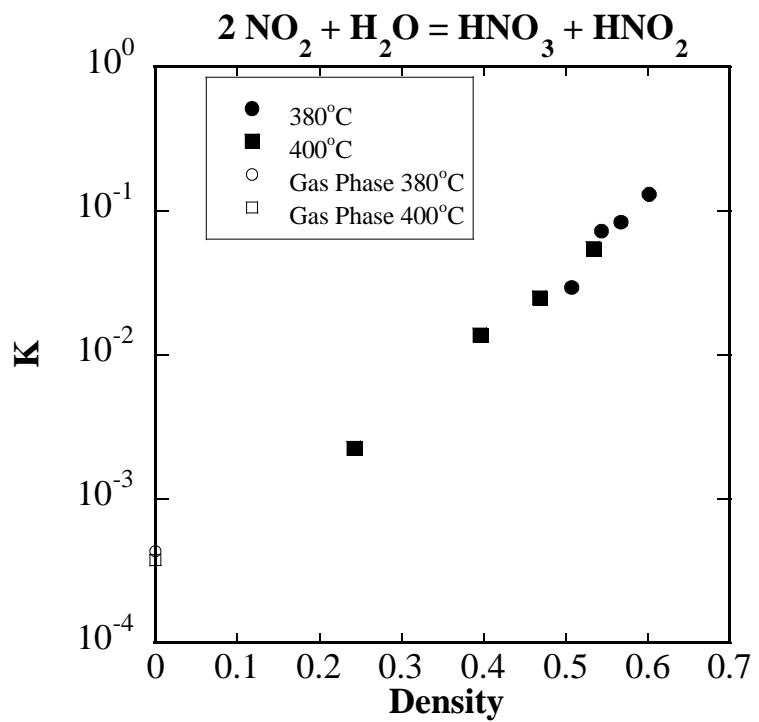
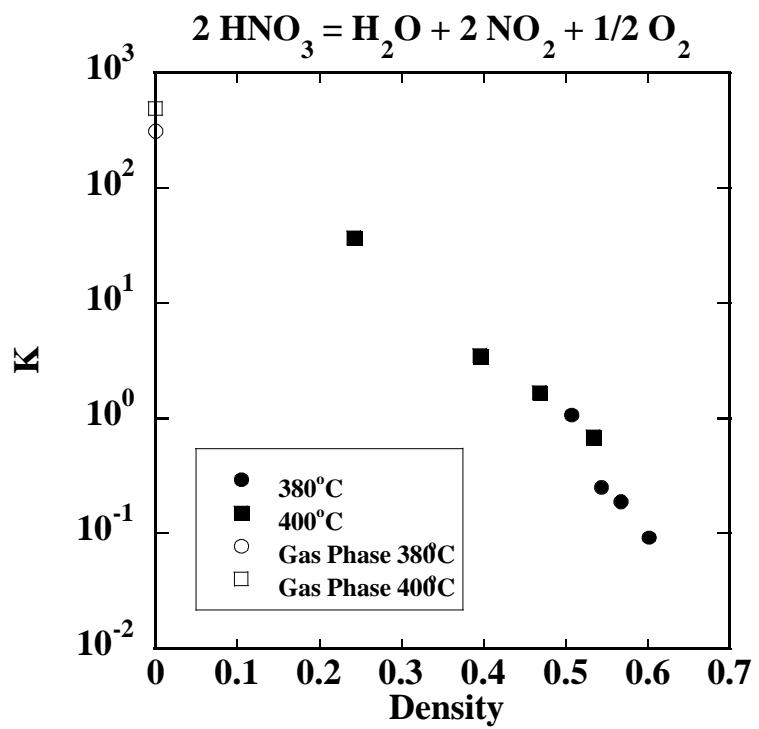
Lines: modified Born eq.



NO_2 and HNO_2 peaks for $3.868 \times 10^{-2} \text{ m}$
 HNO_3 in SCW

Pressure (MPa): 27.6 (1); 31.0 (2); 34.5 (3); 41.3 (4).





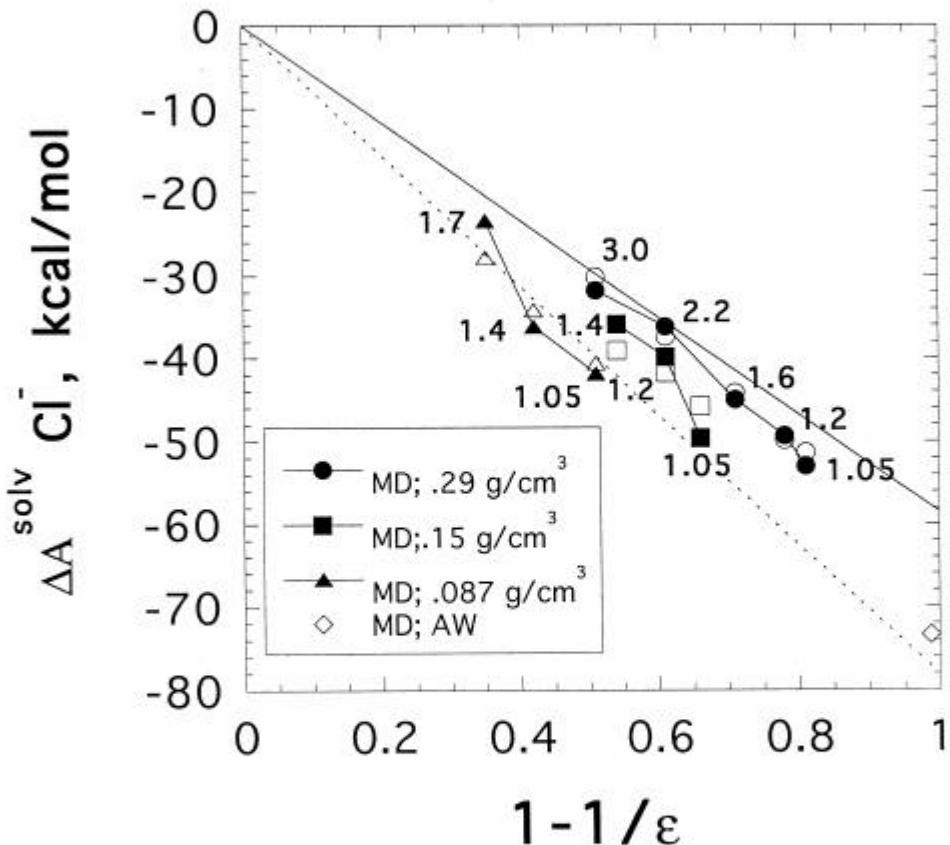
Molec. Dynamics Free Energy Perturbation Comp. Simulation of Reactions and Solvation in SCW

$$\delta A(\lambda) = -kT \ln \{ \exp[-(U_{SW}(\lambda + \delta\lambda) - U_{SW}(\lambda))/kT] \}_\lambda$$

Relevance

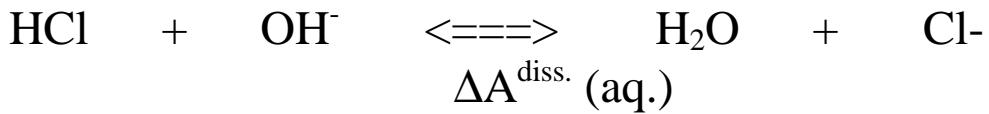
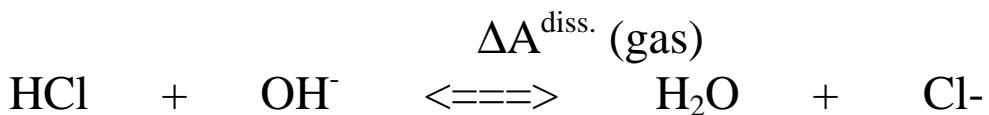
1. Provide detailed picture of water molecules along reaction coordinate in a condensed phase-not experimentally available
2. Bridge gap between intermolecular forces and:
 - solvation
 - solvent effect on rxn, rate and equilibrium constants
3. Basis to develop and test molecular thermodynamic models
4. Guide and interpret spectroscopic studies
5. Role of clustering (solvation) of water molecules comparison with continuum models and expt.

MD vs CSM
(local densities from simulations)



Energies and entropies of solvation (ions + molecules) and ΔA^{diss} for $\text{HCl} + \text{OH}^- = \text{H}_2\text{O} + \text{Cl}^-$ (units: kcal/mol).

T(K)	Density (g/cm ³)	ΔE^{solv} (ions + molec.)	$-\text{T}\Delta S^{\text{solv}}$ (ions + molec.)	$\Delta A^{\text{diss.}}$ (gas)	$\Delta A^{\text{diss.}}$ (aq.)	ΔpK^* (gas)	ΔpK^* (aq.)
298.	0.997	12.0	0.9	-56.0	-43.1	-41.1	-31.6
673.	0.290	13.4	-0.9	-53.7	-40.1	-17.5	-13.6



Aqueous ion transport properties from water reorientational dynamics

Friction coefficient

$$\frac{1}{\zeta} = \int_{R_l}^{\infty} \frac{dr}{s p r^2 h(r)}$$

$$h(r) = h_{bulk} \equiv h \quad \text{for} \quad r > R_c$$

$$h(r) = h_s \quad \text{for} \quad r < R_c$$

$$\frac{1}{\zeta} = \frac{1}{sphR_l} \left\{ \frac{h}{h_s} + \frac{R_l}{R_c} \left(1 - \frac{h}{h_s} \right) \right\}$$

Dipole reorientation time

$$\tau_{ion}^R = \frac{8\pi\eta_s R^3}{kT}$$

$$\tau_{bulk}^R = \frac{8\pi\eta R^3}{kT}$$

$$\frac{1}{\zeta} = \frac{1}{sphR_l} \left\{ \frac{\tau_{bulk}^R}{\tau_{ion}^R} + \frac{R_l}{R_c} \left(1 - \frac{\tau_{bulk}^R}{\tau_{ion}^R} \right) \right\}$$

Time-correlation function for dipole reorientation

$$c_l(t) = \left\langle P_l(\underline{u}_i(t + t_o) \bullet \underline{u}_i(t_o)) \right\rangle_{t_o}$$

where \underline{u}_i is a unit vector that characterizes orientation

P_l : Legendre polynomial of degree l

$$\mathbf{t} = \int_0^{\infty} c(t) dt$$

Conductivity

$$\Lambda_0 = \text{Fe}/\zeta$$

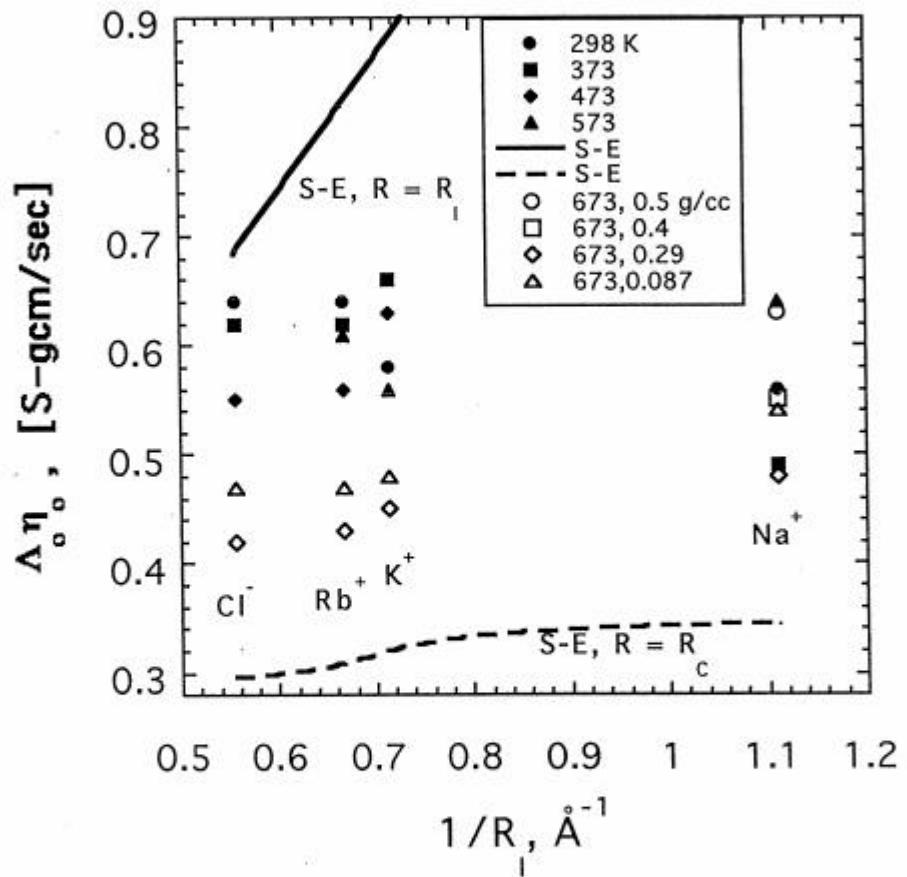
Diffusion coefficient

$$D = kT / \mathbf{z}$$

Walden product

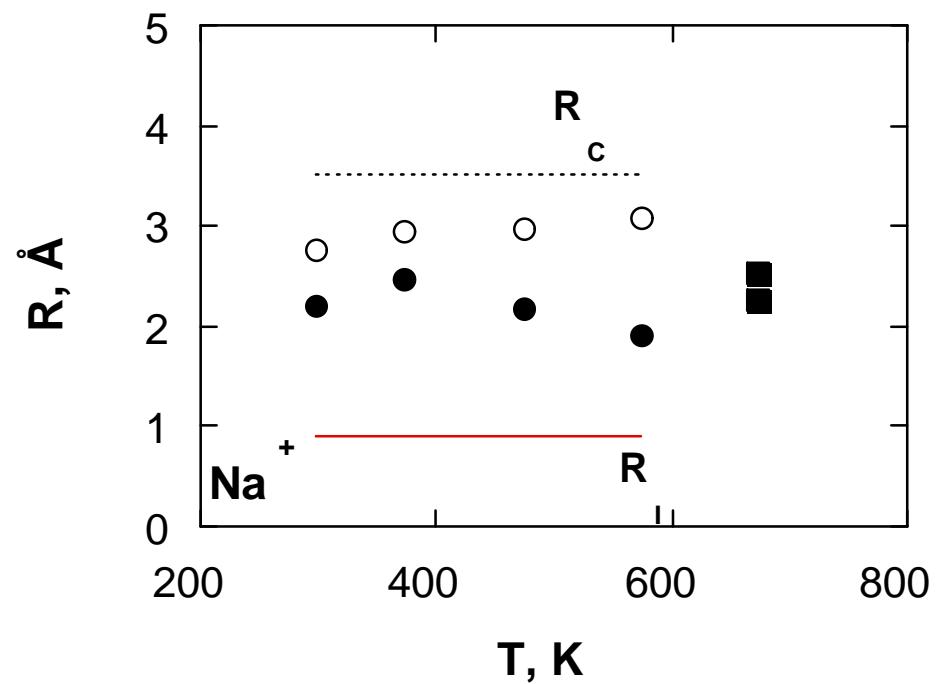
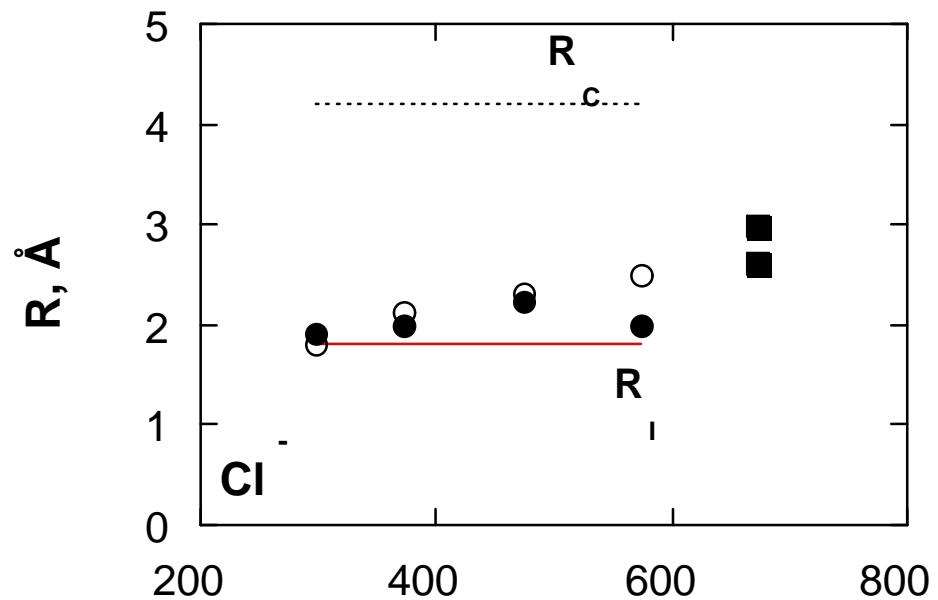
$$\Lambda_0 \eta = \text{Fe}/(\zeta/\eta)$$

Walden Products for Ions in Aqueous Solution at Sub- and Supercritical Conditions



Effective Stokes-Einstein radii for Cl⁻ and Na⁺

filled- calculated open: exp, Oelkers and Helgeson, 1989.



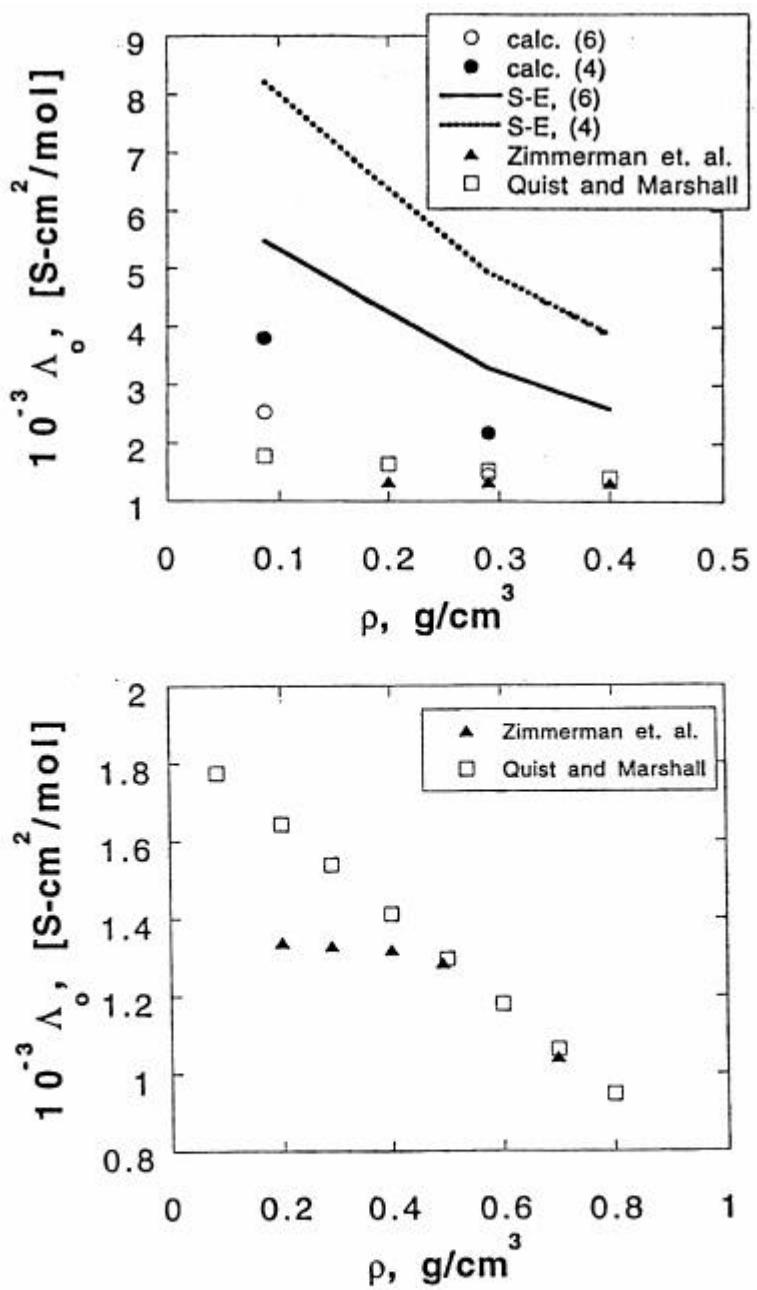


Figure 5. Limiting equivalent conductance for NaCl at 673 K

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