Polarity and hydrogen-bonding of ambient to near-critical water: Kamlet–Taft solvent parameters

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The Kamlet–Taft solvent parameters π^*, α, and β of saturated liquid water have been determined from 25 to 275 °C based on solvatochromic measurements and indicate that the polarity and hydrogen-bonding of water are highly tunable properties with temperature.

Nearcritical water (NCW) is an environmentally benign solvent and alternative reaction medium, which can simultaneously solubilize organics and ionics[1] because the dielectric constant of water decreases significantly at elevated temperatures (for example, ε = 23.5 at 275 °C).[2] In addition, the ionization constant of water increases several orders of magnitude from ambient to nearcritical conditions,[3] providing hydronium and hydroxide ions that can act as modest acid or base catalysts in chemical reactions.[4,5] Interest in NCW as a reaction medium has prompted study of the solvent properties of water at elevated temperature.[6,7] However, to date our understanding of the solvent properties of NCW has been inadequate for correlating and predicting chemical reactions and other physicochemical processes.

Kamlet–Taft solvent parameters π^*, α, and β have been related to a variety of configurational properties in solution: solubilities, partition coefficients, thermodynamic and kinetic properties of chemical reactions, *etc.*, based on successful treatments of solvent effects by linear solvation energy relationship (LSER) theory,[8]

$$\mathrm{XYZ} = (\mathrm{XYZ})_0 + s\pi^* + a\alpha + b\beta$$

where π^*, α and β are the parameters for dipolarity/polarizability, hydrogen bond donating ability and hydrogen bond accepting ability, respectively. XYZ and $(\mathrm{XYZ})_0$ are the solvent-dependent physicochemical properties in a given solvent and in a reference solvent (gas or inert solvent). s, a, and b are solvent-independent coefficients indicating the susceptibility of the corresponding parameters to the solvent property. Based on the LSER theory, the π^*, α, and β solvent parameters of water can be used to correlate and predict processes occurring in NCW. In this work, we report the solvatochromic parameters of saturated liquid water in the temperature range 25–275 °C.

A high-pressure titanium optical cell equipped with sapphire windows (Insaco Inc., PA, 0.50 inches diameter, 0.25 inches thick) sealed with gold gaskets (Aldrich, 99.99%) was constructed to measure the solvatochromic parameters of NCW from ambient to nearcritical conditions. The path length of the cell is 10.5 mm at rt and the internal volume is 17.7 cm^3.

Some of the indicators used decompose in water at elevated temperatures. When decomposition products contain similar chromophores to those of indicators, an undesirable spectral shift can result. In order to avoid errors associated with decomposition of solvatochromic indicators, the cell was first loaded with water (Aldrich, HPLC grade, deoxygenated with N_2 before being used) and heated to the desired temperature. Then a small amount of concentrated indicator solution was injected into the cell through a sample loop. Temperature equilibrium was restored within 10 s. Multiple spectra were measured in less than five minutes before significant decomposition could take place. A Hewlett-Packard 8450 UV-Vis spectrophotometer was used to perform the spectroscopic measurements and data processing.

The π^* parameters were determined based on the UV-Vis spectral shift of 4-nitroanisole (Aldrich, 97%). Cyclohexane and dimethyl sulfoxide at ambient conditions were used as reference solvents, the π^*s of which are 0.0 and 1.0, respectively.

The spectral shift of the dichloro-substituted betaine dye (2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate, Fluka, HPLC grade) was measured to obtain α parameters instead of commonly used betaine dye. To function as an effective solvatochromic indicator, a betaine dye must remain deprotonated. The p*K*a of the betaine dye ($E_T(30)$ dye) is 8.6,[9] while that of dichloro-substituted betaine dye ($E_T(33)$ dye) is 4.8. The latter is less basic and a more suitable indicator for this study due to the increased ionization constant of water at nearcritical conditions. The $E_T(30)$ values of water were obtained from the established correlation between $E_T(30)$ and $E_T(33)$.[9] The calculation of α is based on the correlation with $E_T(30)$ and π^*, which is deduced from the correlation of literature data of 16 compounds.[10] 4-nitroaniline (Aldrich, 99+%) and *N*,*N*-dimethyl-4-nitroaniline (Acros) were used to obtain the β based on the solvatochromic comparison method.[11]

The π^* values of water are shown at different temperatures from 25 to 275 °C in Fig. 1. The dipolarity/polarizability of water decreases continuously with increasing temperature. At 275 °C, water has a polarity comparable to that of acetic acid at rt. This trend is consistent with the decrease in the dielectric constant of water with temperature as observed by Uematsu and Franck.[2]

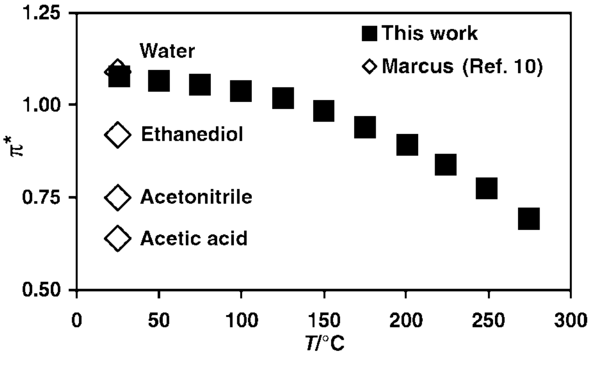

Fig. 1 π^* for nearcritical water as a function of temperature.

α indicates the hydrogen bond donating ability of a solvent. The α values of saturated liquid water as a function of temperature are shown in Fig. 2. The hydrogen bond donating ability of water decreases at elevated temperature and changes from that of ambient water to ambient methanol-like and then to ambient ethanol-like when we raise the temperature from 25 to 275 °C.

β indicates the hydrogen bond accepting ability of a solvent. The β values of water are shown in Fig. 3. Although various values of β are reported in the literature, this result at rt is consistent with that of Taft *et al.*, who attributed it to water-

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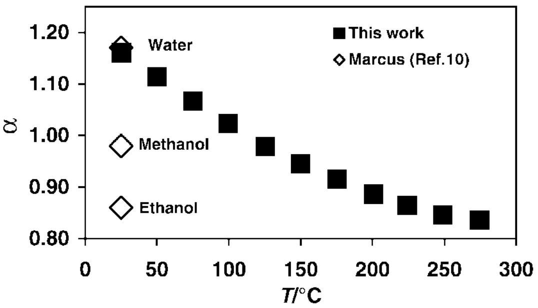

Fig. 2 α for nearcritical water as a function of temperature.

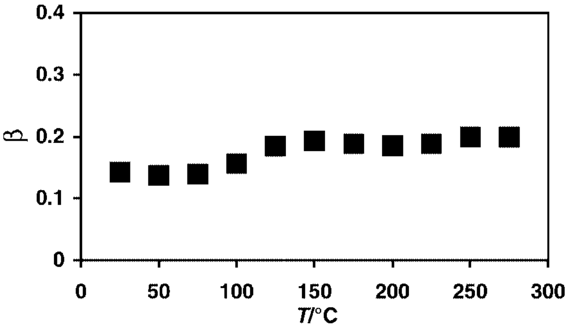

Fig. 3 β for nearcritical water as a function of temperature.

solvent clusters.[12] In contrast to the π^* and α of water, the β actually increases slightly with increasing temperature. The slight increase of β may be brought about by the breakdown of the hydrogen-bonding network of water at elevated temperature, which makes the oxygen atom of the water molecule more accessible as a hydrogen bond acceptor.[13] Bennett and Johnston measured the solvatochromism behavior of organic probes in near- and supercritical water, and observed similar large changes in polar and hydrogen-bonding interactions as the temperature was increased from ambient to 250 °C.[6]

In summary, the large dipolarity/polarizability, π^*, and hydrogen bond donating ability, α, of ambient water decrease significantly with increasing temperature. The hydrogen bond accepting ability, β, remains low and relatively constant throughout the entire temperature range studied. NCW is a benign and promising reaction medium for the replacement of organic solvents. The Kamlet–Taft parameters we report in this work provide a powerful tool for describing varied physicochemical processes in NCW.

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