Deuterium Isotope Effects, $\Delta pK = pK_{D2O} - pK_{H2O}$, on the Second Dissociation of Carbonic Acid by Raman Spectroscopy

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An Undergraduate Level Submission

Summary

Polarized Raman spectroscopy has been used to measure the deuterium isotope effect, $\Delta pK = pK_{D2O} - pK_{H2O}$, for the second ionization constant of carbonic acid in the temperature range of 25 °C to 125 °C, $CO_3^{2-} + D_2O \leftrightharpoons DCO_3^- + OD^-$. Results for the light water p*K* dependence on temperature were compared to literature, confirming the reliability of the method.

1. Introduction

The Canadian designed CANDU reactor system employs a unique heat transport technology; in the reactor, heavy water is used both as the moderator and the heat-transfer fluid in the primary coolant loop. The chemical behaviour of metal oxides, dissolved gases and pH control agents in high temperature D_2O must be understood in order to design operating strategies that minimize corrosion and the transport of radioactive corrosion products in the primary loop. Currently, experiments used to optimize operating conditions are performed in light water in pressure vessels or in small-scale, high-pressure pilot loops [1]. In order to better calibrate operating conditions, the physical properties of chemicals in D_2O and the manner in which these properties differ in H_2O at high temperature, up to 573 K, must be determined.

Only a few systems have had ionization or metal ion hydrolysis studies performed on them in heavy water at high temperature and pressure [2-5]. Shoesmith and Lee [3] and Mesmer and Herting [4] have determined the self-ionization of D_2O at high temperature by electrochemical techniques. Mesmer and Herting also determined the dissociation constant of $D_2PO_4^-$ at temperatures up to 573 K [4]. Lietske and Stoughton determined the DSO_4^- ionization constant from solubility measurements of Ag_2SO_4 in D_2SO_4 solutions from 298 to 498 K [5]. More recently, Erikson *et al.* [2, 6] determined the deuterium isotope effect on the dissociation of acetic acid and phosphoric acid by AC conductance (Figure 1). There does not currently seem to be an existing model to estimate deuterium isotope effects at elevated temperature and pressure.

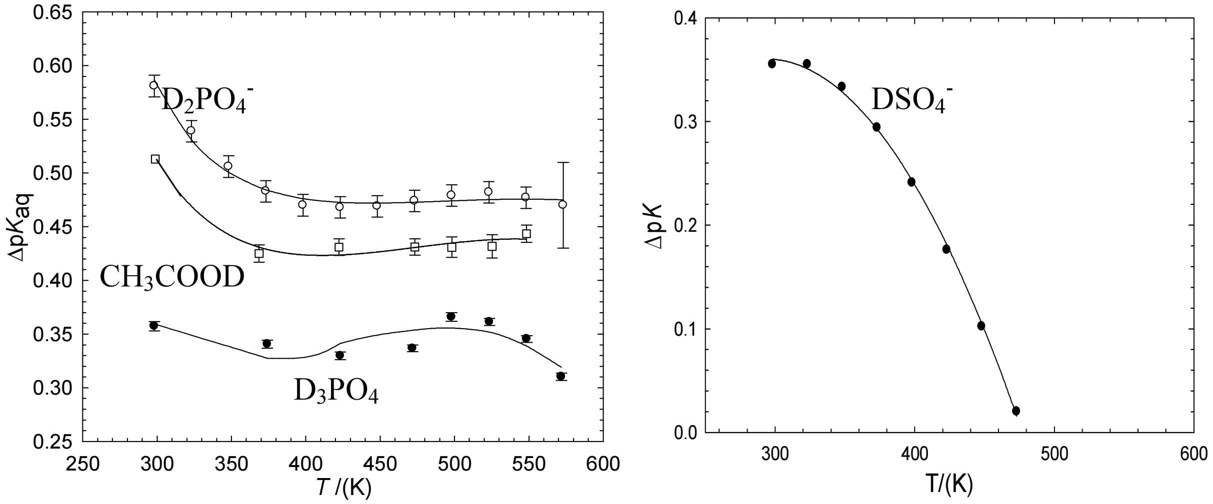

Figure 1. The deuterium isotope effect on ionisation of $D_2PO_4^-$ [4], CH_3COOD [2], D_3PO_4 and DSO_4^- [5].

2. The Second Dissociation of Carbonic Acid by Raman Spectroscopy

This study has researched the isotope effect for the dissociation of bicarbonate to add the knowledge base of the systems for which the deuterium isotope effect is known at high temperature. The ionization constant of the bicarbonate / carbonate system has already been measured in light water up to 492 K by Rudolph *et al.* [7] using Raman spectroscopy. In this study, polarized Raman spectroscopy was used to determine quantitative equilibrium constants (K_h) for the hydrolysis of the carbonate ion in light and heavy water [Eqn. 1.] at 25, 80 and 125 °C (Figure 2), using solutions of Na_2CO_3 and K_2CO_3 at molalities of 0.32, 0.10, and 0.05 mol kg^{-1} in light and heavy water.

$$CO_3^{2-} + D_2O \rightleftharpoons DCO_3^- + OD^-$$

$$K_{2,OD} = \frac{m_{DCO_3^-} m_{OD^-}}{m_{CO_3^{2-}}} \tag{1}$$

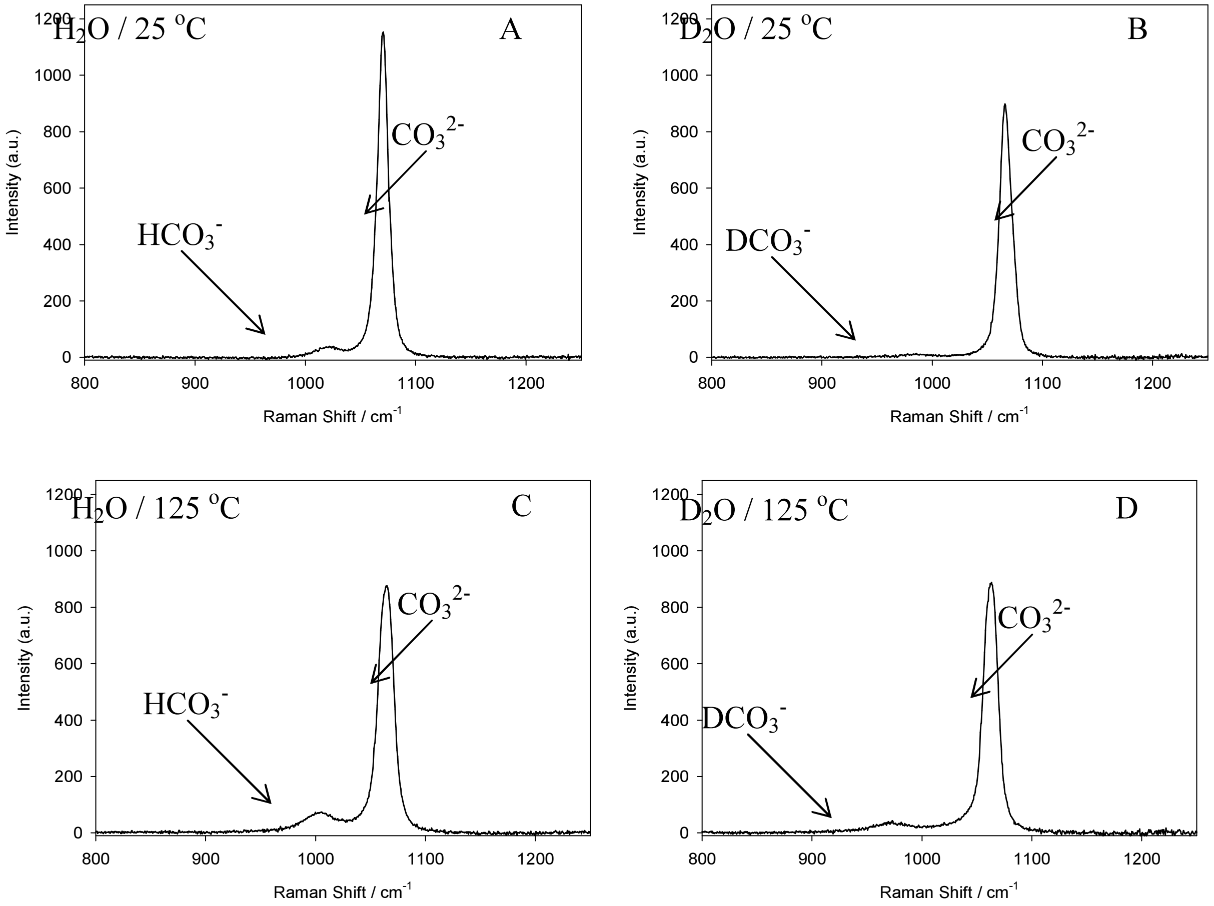

Figure 2. Reduced Raman spectra of 0.32 molal K_2CO_3 in H_2O at 25 °C and 125 °C (A and C) and D_2O at 25 °C and 125 °C (B and D).

The relative abundance of the carbonate and bicarbonate species in solution was determined, by measuring the ratio of the areas of the carbonate symmetric stretching band at 1066 cm^{-1} and the bicarbonate C-OH stretching band at 1016 cm^{-1}. From the calculated concentrations, the equilibrium constants for the hydrolysis of carbonate in both light and heavy water were determined, and by extension, the equilibrium constants for the dissociation of bicarbonate and deuterated bicarbonate [Eqn. 2.] at 25, 80, and 125 °C. The calculated equilibrium constants have been used to determine the deuterium isotope effect, $\Delta pK_2 = pK_{2,D_2O} - pK_{2,H_2O}$, for the second dissociation reaction of carbonic acid at each temperature (Figure 3).

$$DCO_3^{-} \rightleftharpoons CO_3^{2-} + D^{+} \qquad (2)$$

$$K_2 = \frac{K_{2,OD}}{K_W}$$

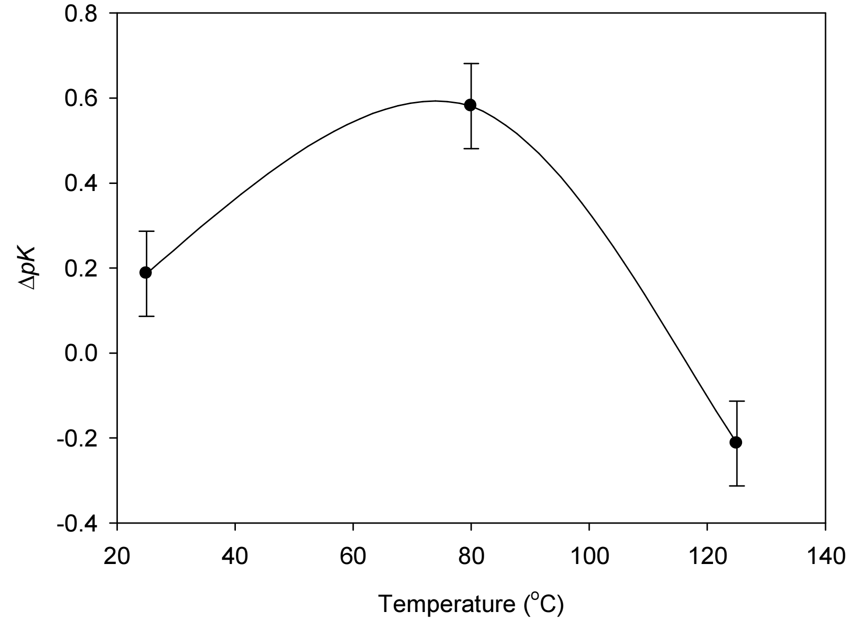

Figure 3. Difference in the pK for the dissociation reaction of bicarbonate in light and heavy water as a function of temperature.

At 125 °C and, to a lesser extent at 80 °C, silicate from dissolution of quartz sample tubes was observed in the Raman spectra. In order to quantify the amount of dissolved silicate and thereby correct for it, the Raman scattering efficiency of silicate was determined by acquiring Raman spectra of tetramethyl ammonium silicate (TMAS) solutions and solutions of TMAS spiked with a known concentration of Na_2CO_3. Determination of the amount of silicate present in our solution samples allows the equilibrium constants to be duly adjusted for the decrease in pH caused by the H_4SiO_4 / $H_3SiO_4^-$ equilibrium.

3. References

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