THE JOURNAL OF
PHYSICAL
CHEMISTRY A

© Copyright 2004 by the American Chemical Society VOLUME 108, NUMBER 10, MARCH 11, 2004

LETTERS

Effects of Na_2SO_4 and $NaClO_4$ on the Molecular Organization of H_2O

Yoshikata Koga,*,[†,‡] Peter Westh,[‡] and Keiko Nishikawa[§]

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1, Department of Biological Sciences and Chemistry, Roskilde Universitycenter, Roskilde DK-4000, Denmark, and Graduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan

Received: November 14, 2003

We study thermodynamic behaviors of 1-propanol (abbreviated as 1P) in ternary 1P−salt−H_2O in order to elucidate the effects of salt on the molecular organization of H_2O. We determine the excess partial molar enthalpy of 1P, H_{1P}^E, as a function of the mole fraction of 1P, x_{1P}, and the salt. We examine the x_{1P} dependence of H_{1P}^E, and changes induced by the presence of salt are used to elucidate the effect of the salt on the molecular organization of H_2O. We previously found that an NaCl ion pair binds 7 to 8 molecules of H_2O, but has no effect on H_2O outside of the hydration shell. Na_2SO_4 and $NaClO_4$, on the other hand, modify the molecular organization of H_2O each in different ways. In particular, ClO_4^- seems to participate in the hydrogen bond network of H_2O and to retard the degree of fluctuation inherent in liquid H_2O.

Omta et al. in a recent article[1] concluded that the addition of $Mg(ClO_4)_2$, $NaClO_4$, or Na_2SO_4 has no effect on the rotational dynamics of H_2O molecules outside the first hydration shell, by means of femto second pump−probe spectroscopy. This observation is potentially of great importance, since SO_4^{2-} and ClO_4^- are known to have strong effects on respectively kosmotropic and chaotropic properties.[2] Therefore, direct dynamic information on aqueous solutions of these ions could be useful for molecular level understandings of the ubiquitous, but still poorly understood, Hofmeister effects.[2−4] In this letter, we report thermodynamic data suggesting that, although NaCl, which exhibits weak chaotropic/kosmotropic effects, has indeed no effect, $NaClO_4$ and Na_2SO_4 do have qualitatively different effects on the molecular organization of H_2O. Our strategy[5−7] is to determine the excess partial molar enthalpy of 1-propanol (1P) in a 1P−salt−H_2O system. We titrate a small enough potion of 1P successively into a mixed solvent of salt + H_2O. For each titration, we determine the thermal response of the system and obtain the excess partial molar enthalpy of 1P, H_{1P}^E, a change in enthalpy of the entire system per mole of added 1P. Thus, H_{1P}^E provides information about the actual enthalpic situation of 1P in the mixture. The composition dependence of H_{1P}^E thus determined, or the slope of the tangent at a given mole fraction of 1P, x_{1P}, signifies the effect of additional 1P on the actual enthalpic situation of existing 1P. We name this quantity as the enthalpic interaction, H_{1P-1P}^E, which provides a measure of the 1P−1P interaction in terms of enthalpy. This information is obtained purely experimentally and is completely free from presumption inherent in any model system.

We then inspect the x_{1P} dependence of H_{1P-1P}^E on addition of a salt. The resulting changes on H_{1P-1P}^E and on its x_{1P} dependence are used as a probe to elucidate the effect of an added salt on the molecular organization of H_2O. As explained briefly below, this methodology was powerful in elucidating the effect of NaCl on the molecular organization of H_2O. Namely, we showed earlier[8] that an Na^+ and a Cl^- ions bind the total of 7−8 molecules of H_2O but leave the bulk H_2O away

---

* To whom correspondence should be addressed. Phone: (604) 822-3491. Fax: (604) 822-2847. E-mail: koga@chem.ubc.ca.

[†] The University of British Columbia.

[‡] Roskilde Universitycenter.

[§] Chiba University.

10.1021/jp031247w CCC: $27.50 © 2004 American Chemical Society
Published on Web 02/14/2004

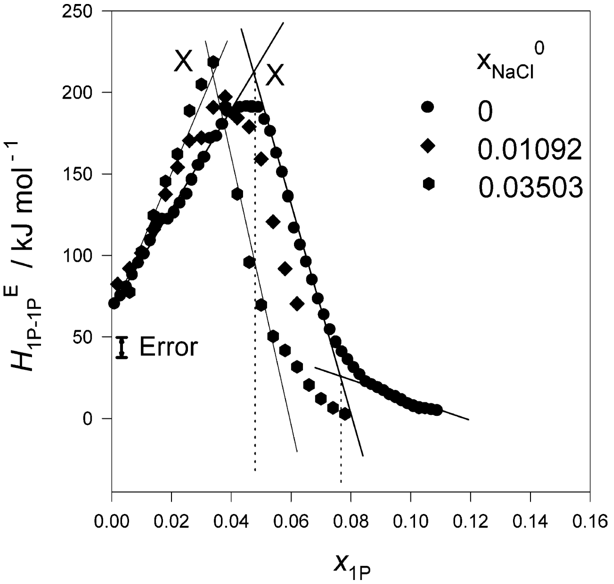

Figure 1. Enthalpic interaction H_{1P-1P}^E in 1-propanol−NaCl−H_2O at 25 °C, as a function of mole fraction of 1-propanol, x_{1P}, given the initial mole fraction of NaCl, x_{NaCl}^0. In the region from $x_{1P} = 0$ to point X, H_2O keeps the hydrogen bond percolation nature.

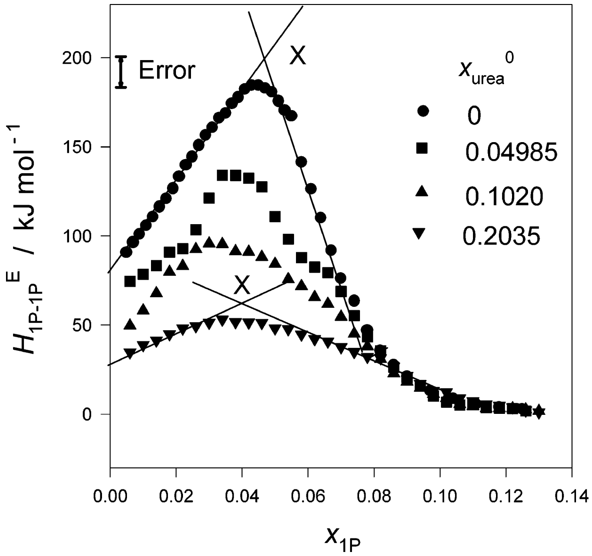

Figure 2. Enthalpic interaction H_{1P-1P}^E in 1-propanol−urea−H_2O at 25 °C, as a function of mole fraction of 1-propanol, x_{1P}, given the initial mole fraction of urea, x_{urea}^0. In the region from $x_{1P} = 0$ to point X, H_2O keeps the hydrogen bond percolation nature.

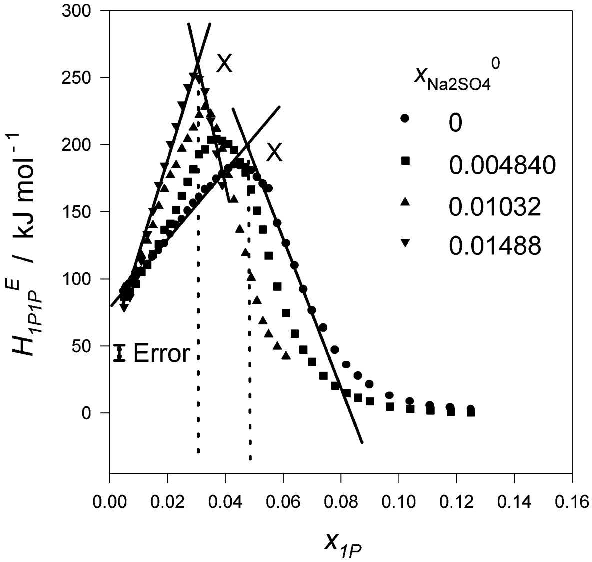

Figure 3. Enthalpic interaction H_{1P-1P}^E in 1-propanol−Na_2SO_4−H_2O at 25 °C, as a function of mole fraction of 1-propanol, x_{1P}, given the initial mole fraction of Na_2SO_4, x_{Na2SO4}^0. In the region from $x_{1P} = 0$ to point X, H_2O keeps the hydrogen bond percolation nature.

from NaCl ions unaltered. This is in complete accordance with the conclusion by a first principle simulation study.[9] However, our recent studies using the same methodology on Na_2SO_4 and $NaClO_4$ indicate that their effects are different from each other and in turn different from that by NaCl.

Figure 1 shows the enthalpic interaction, H_{1P-1P}^E, in 1P−NaCl−H_2O.[8] The region from the start at $x_{1P} = 0$ to point X in the figure describes the process of 1P modifying the molecular organization of H_2O. In this region, 1P enhances the hydrogen bond network of H_2O in its immediate vicinity. At the same time, the hydrogen bond probability of bulk H_2O away from 1P is progressively reduced.[5−7] However, one of the characteristics of liquid H_2O that the hydrogen bond network is bond-percolated[10] is still retained. This proceeds to point X whereupon the hydrogen bond probability of bulk H_2O away from 1P is reduced to the percolation threshold of ice Ih bond connectivity, and the percolation nature of the network is lost. A new mixing scheme pertinent in the intermediate region sets in.[5−7] As is evident in Figure 1, addition of NaCl shifts point X to a smaller value of x_{1P} without changing the value of H_{1P-1P}^E, in comparison with the uncertainty. Its value at $x_{1P} = 0$ also remains unchanged.

Earlier we observed[11] that the x_{1P}-dependence of H_{1P-1P}^E and that of the partial molar entropy-volume cross fluctuation calculated using thermal expansivity data are identical in a relative scale. This suggests that the underlying mechanism for the x_{1P}-dependence of H_{1P-1P}^E and that of the partial molar entropy-volume cross fluctuation share the same cause. One of the characteristics of liquid H_2O manifests itself in a negative contribution in the entropy-volume cross fluctuation due to putative formation/destruction of ice-like patches in addition to the positive part as normal liquids. Hence, the increase in H_{1P-1P}^E is associated with the decrease of the negative contribution or the increase in the positive part in the cross fluctuation. Returning to Figure 1, the shift of point X to a smaller value of x_{1P} suggests that the presence of NaCl retards the availability of H_2O toward 1P for the latter to drive the system to point X. From the proportionality factor, about 7.5 molecules of H_2O are bound to one ion pair of NaCl and are protected from interacting with 1P. From the fact that the values of H_{1P-1P}^E and hence of the partial molar entropy-volume cross fluctuation were independent of the NaCl concentration both at $x_{1P} = 0$, and the end point, point X, we concluded that NaCl has very little effect on the molecular organization of H_2O beyond the hydration shell.[8]

Figure 2 shows the same type of graph for 1P−urea−H_2O.[12] The fact that the locus of point X remains almost unchanged suggests that the percolated network of hydrogen bonding remains intact in the presence of urea. However, the value of H_{1P-1P}^E and hence the degree of fluctuation inherent in liquid H_2O is retarded. Thus, urea seems to participate in forming the hydrogen bond network of H_2O and to reduce the degree of fluctuation by breaking the proton donor/acceptor symmetry in pure H_2O. Another simulation study[13] concluded that urea leads to stiffening of the short-time dynamics of both urea and H_2O.

Figures 3 and 4 show our recent analogous results for Na_2SO_4 and $NaClO_4$. The behaviors of the x_{1P} dependence of H_{1P-1P}^E for either case are quite different from that for NaCl. Thus,

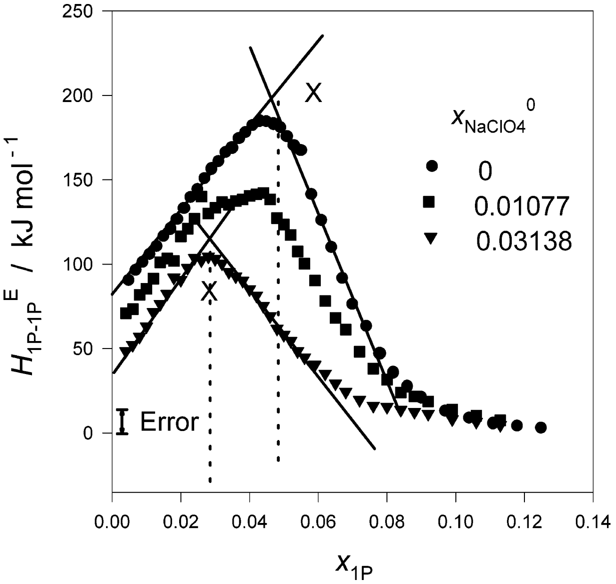

Figure 4. Enthalpic interaction H_{1P-1P}^E in 1-propanol$-$NaClO$_4$$-H_2$O at 25 °C, as a function of mole fraction of 1-propanol, x_{1P}, given the initial mole fraction of NaClO$_4$, $x_{NaClO4}°$. In the region from $x_{1P} = 0$ to point X, H$_2$O keeps the hydrogen bond percolation nature.

contrary to the claim by Omta et al.,[1] Na$_2$SO$_4$ and NaClO$_4$ seem to modify the molecular organization of H$_2$O. The shifts of point X to smaller values of x_{1P} may partly be due to Na$^+$ ions in both salts. However, for NaClO$_4$, its effect is closer to that of urea, whereas Na$_2$SO$_4$ seems to either retard the negative contribution of the cross fluctuation strongly or to increase the normal positive part of the entropy-volume cross fluctuation. SO$_4^{2-}$ and ClO$_4^-$ ions are in almost at the opposite end of the Hofmeister series.[2–4] Thus, it is natural that their effects on H$_2$O could be qualitatively different. A fuller account including other salts in the Hofmeister series is forthcoming. Attempts at correlating these types of plots (H_{1P-1P}^E vs x_{1P}) to the mechanism underlying Hofmeister effects await the accumulation of more data for comparative analysis.

Materials and Methods

Na$_2$SO$_4$ (AnalaR, Analytical Reagent, BDH) and NaClO$_4$ (Fluka, >99.0%) were used as supplied. Stock solutions were made by weighing in a dry atmosphere and successively diluted by weight as required. 1-Propanol (ACROS Organics, 99.5%) and (Fluka, 99.8%) as supplied were treated in a dry nitrogen atmosphere.

The excess partial molar enthalpies of 1P, H_{1P}^E, for Na$_2$SO$_4$ were determined by a homemade titration calorimeter of a similar design to an LKB Bromma 8700.[14] The uncertainty is estimated as ±0.03 kJ mol^{-1}. For NaClO$_4$, a TAM titration calorimeter was used. The uncertainty is ±0.005 kJ mol^{-1}. The value of $H_{1P}^E = (\partial H^E/\partial n_{1P})$ is approximated as $(\delta H^E/\delta n_{1P})$, where δH_{1P}^E is the determined thermal response of the system on titratng a small amount δn_{1P}. The goodness of this approximation is tested by changing the size of δn_{1P} and by checking that the quotient $(\delta H^E/\delta n_{1P})$ converges. About 1 mol % of δn_{1P} to the total mole in the cell seems satisfactory.[15] The uncertainties quoted above are obtained considering this procedure. The resulting data of H_{1P}^E are plotted on a graph. The data points are typically in the increment in mole fraction of 1P, $\delta x_{1P} = 0.003$. We then draw the best smooth curve through all of the data points by aide of a flexible ruler, and read the value off the curve drawn at a chosen interval δx_{1P}. The enthalpic interaction, H_{1P-1P}^E, is defined as, $H_{1P-1P}^E = N(\partial H_{1P}^E/\partial n_{1P}) = (1 - x_{1P})(\partial H_{1P}^E/\partial x_{1P})$. The last derivative is then approximated by $(\delta H_{1P}^E/\delta x_{1P})$, where δH_{1P}^E is the difference in H_{1P}^E read off at a given interval δx_{1P}. The most appropriate size of δx_{1P} for the best approximation was determined to be 0.01 earlier by trial and error.[16] The caution against the method of curve fitting a function to H_{1P}^E vs x_{1P} data and arithmetically differentiating the fitted function is given earlier.[5] Thus, we now obtained H_{1P-1P}^E data purely experimentally and are completely free from presumptions inherent in a fitting function.

Acknowledgment. This research was supported by Natural Science and Engineering Research Council of Canada, the Carlsberg Foundation, Danish Research Council, and Ministry of Education, Science and Culture, Japan.

References and Notes

(1) Omta, A. W.; Kropman, M. F.; Wouterse, S.; Bakker, H. J. *Science* **2003**, *301*, 347.

(2) Cacace, M. G.; Landau, E. M.; Ramsden, J. J. *Quart. Rev. Biophys.* **1997**, *30*, 241.

(3) Lewith, S. *Naunyn-Schmiedebegs Arh. Exp. Pathol. Pharmacol.* **1888**, *23*, 1.

(4) Hofmeister, F. *Naunyn-Schmiedebegs Arh. Exp. Pathol. Pharmacol.* **1888**, *23*, 247.

(5) Koga, Y. *J. Phys. Chem.* **1996**, *100*, 5172.

(6) Koga, Y. *Netsusokutei (J. Jpn. Soc. Cal. Therm. Anal.)* **2003**, *30*, 54. (Available in a pdf format on request to the author).

(7) Koga, Y. *J. Therm. Anal. Cal.* **2002**, *69*, 705.

(8) Matsuo, H.; To, E. C. H.; Wong, D. C. Y.; Sawamura, S.; Taniguchi, Y.; Koga, Y. *J. Phys. Chem. B* **1999**, *103*, 2981.

(9) White, J. A.; Schwegler, E.; Galli, G.; Gygi, F. *J. Chem. Phys.* **2000**, *113*, 4668.

(10) Stanley, H. E.; Teixeira, J. *J. Chem. Phys.* **1980**, *73*, 3404.

(11) Koga, Y. *Can. J. Chem.* **1999**, *77*, 2039.

(12) To, E. C. H.; Hu, J.; Haynes, C. A.; Koga, Y. *J. Phys. Chem. B* **1998**, *102*, 10958.

(13) Idrissi, A.; Sokolic, F.; Perera, A. *J. Chem. Phys.* **2000**, *112*, 9479.

(14) Koga, Y. *Can. J. Chem.* **1988**, *66*, 1187.

(15) Koga, Y. *J. Chem. Thermodyn.* **1987**, *19*, 571.

(16) Parsons, M. T.; Westh, P.; Davies, J. V.; Trandum, Ch.; To, E. C. H.; Chiang, W. M.; Yee, E. G. M.; Koga, Y. *J. Solution Chem.* **2001**, *30*, 1007.