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Toward Understanding the Hofmeister Series. 1. Effects of Sodium Salts of Some Anions on the Molecular Organization of H_2O

Yoshikata Koga,[*,†,‡] Peter Westh,[§] James V. Davies,[‖] Kumiko Miki,[§,⊥] Keiko Nishikawa,[#] and Hideki Katayanagi[○]

Department of Chemistry, The University of British Columbia, Vancouver, B.C., Canada V6T 1Z1, Suiteki Juku (Water Drop Institute), Vancouver, B.C., Canada V6R 2P5, Department of Life Science and Chemistry, Roskilde University, Roskilde, DK-4000 Denmark, Department of Chemistry, The University College of the Cariboo, Kamloops, B.C., Canada V2C 5N3, Department of Liberal Arts and Basic Sciences, College of Industrial Technology, Nihon University, Narashino-shi, Chiba 275-8575, Japan, Graduate School of Science and Technology, Chiba University, Chiba 263-8522, Japan, and Center for Frontier Electronics and Photonics, Chiba University, Chiba 263-8522, Japan

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We studied a detailed thermodynamic behavior of 1-propanol (abbreviated as 1P) in mixed solvents of aqueous Na_2SO_4, $NaOOCCH_3$, and $NaClO_4$, and NaSCN. We measured the excess partial molar enthalpy of 1P, H_{1P}^{E}, in these mixed solvents at various initial salt concentrations. We then evaluated what we call the enthalpic interaction, $H_{1P-1P}^{E} = (\partial H_{1P}^{E}/\partial n_{1P})$, where n_{1P} is the amount of 1P. The composition dependence of H_{1P-1P}^{E} changes in a characteristic manner on addition of a specific salt. This induced change in the behavior of H_{1P-1P}^{E} is used to elucidate the effect of the salt on the molecular organization of H_2O. Na^+ ion seems to hydrate a number less than seven or eight molecules of H_2O, leaving the bulk H_2O outside the hydration shell unperturbed. SO_4^{2-} also hydrates a number less than 26 H_2O molecules with a concomitant increase in the degree of fluctuation of the bulk H_2O. Na_2SO_4 as a whole hydrates the total of 26 H_2O. CH_3COO^- ion modifies H_2O in a similar manner as an alcohol. Cl^- ion hydrates a number less than seven or eight H_2O molecules leaving the bulk H_2O in the same state as in pure H_2O. NaCl as a whole hydrates the total of seven or eight molecules of H_2O. ClO_4^- and SCN^- participate in hydrogen bonding with the hydrogen bond network of H_2O keeping its connectivity intact. However, they reduce the degree of fluctuation inherent in liquid H_2O. Thus, each ion has its own unique manner of modifying H_2O, except that ClO_4^- and SCN^- modify H_2O in almost the same way. Therefore, it seems fair to state that the phenomenological net result manifested as the Hofmeister series is due to multifacetted factors working in the holistic manner, and a single or a small number of parameters is not sufficient to explain its effect.

Introduction

Textbooks and review articles are available on the century-old concept of the Hofmeister series.[1−3] Together with introductory remarks in more recent papers on this subject,[4,5] the authors all agree that the molecular level understandings of the Hofmeister effects are still elusive, while the order of the effects of salts is phenomenologically well established.

In the present and the planned subsequent works, we make another attempt at understanding the Hofmeister series by elucidating the effects of cosolute (ions and neutral molecules) on the molecular organization of H_2O. There is little doubt that the main cause of the effect of cosolute on biopolymers, as summarized in the Hofmeister series, is how the nature of H_2O is altered by the cosolute. Here we study ternary systems consisting of 1-propanol (abbreviated as 1P hereinafter), a cosolute and H_2O. We use detailed thermodynamic properties of 1P as a probe to learn indirectly about the effect of the cosolute on H_2O. This methodology follows from our earlier thermodynamic studies of binary aqueous nonelectrolytes using second and third derivatives of Gibbs energy, G.[6−8] Together with other mono-ols, the 1P−H_2O system exhibits a characteristic composition dependence in the third derivative quantities. On adding a third component, this characteristic composition dependence changes depending on the nature of the added third component. The induced change is used to elucidate the effect of the third component on the molecular organization of H_2O. This method has been successful in understanding the effects on H_2O of 2-propanol,[9] 1,2- and 1,3-propanediols,[10] glycerol,[11] urea,[12] and NaCl.[13] These findings were summarized in the Proceedings to the Second International Symposium on the New Frontier of the Thermal Studies of Materials.[14] The success with NaCl has led us to the present project. We limit our attention here to SO_4^{2-}, CH_3COO^- (OAc^-), ClO_4^-, and SCN^- with the countercation fixed at Na^+. Together with our previous work on Cl^-,[13] these anions were chosen to cover the Hofmeister effects, the order being $SO_4^{2-} > CH_3OO^-$ (OAc^-) $> Cl^- > ClO_4^- > SCN^-$ from the kosmotropic (of salting-out) to the chaotropic (of salting-in) end.[1−3] Cl^- is ranked close to the null point of the series. A particular motivation for the present

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[*] Correspondence should be addressed to this author; (604) 822-3491, Fax: (604)822-2847, E-mail: koga@chem.ubc.ca.

[†] The University of British Columbia.

[‡] Suiteki Juku (Water Drop Institute).

[§] Roskilde University.

[‖] The University College of the Cariboo.

[⊥] Nihon University.

[#] Graduate School of Science and Technology, Chiba University.

[○] Center for Frontier Electronics and Photonics, Chiba University.

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thermochemical approach to the Hofmeister effect is the suggestion by Collins and Washbaugh[2] that the enthalpic properties are sensitive to—and in some cases diagnostic of—the kosmo- and chaotropic behavior of salts.

The present work is a fuller account of a recent letter by some of us.[15] The latter rapid communication was prompted by the conclusion that, in aqueous Na_2SO_4, $NaClO_4$, and $Mg(ClO_4)_2$, the orientational dynamics of bulk H_2O outside of the hydration shell of ions remain the same as in pure H_2O. This conclusion was drawn by femtosecond pump−probe spectroscopy.[16] As will be shown in detail below, the effect of SO_4^{2-} on the molecular organization of H_2O is qualitatively different from that of ClO_4^- in terms of our thermodynamic methodology, although we cannot comment on the rotational dynamics of bulk H_2O per se.

Methodology

Our methodology has been described at some length earlier for binary[6−8] and ternary aqueous solutions.[9−14] Briefly, we measure the excess partial molar enthalpy of 1P, H_{1P}^E, in the 1P−cosolute−H_2O system. Namely,

$$H_{1P}^{\ E} \equiv (\partial H^E/\partial n_{1P}) \tag{1}$$

where H^E is the excess enthalpy of the system and n_{1P} is the amount of 1P. The total amount is $N = n_{1P} + n_W + n_3$ where n_W an n_3 are the amounts of H_2O and the cosolute. The partial differentiation is performed by keeping all the other independent variables, p, T, n_W, and n_3, constant. Experimentally, we add a small enough amount of 1P, δn_{1P}, and determine the response of the system in terms of H^E, δH^E, and approximate as, $H_{1P}^E \approx (\delta H^E/\delta n_{1P})$. The validity of this approximation is checked by reducing the size of δn_{1P} and checking if the resultant quotient converges.[17] As the definition, eq 1, implies, H_{1P}^E is the actual enthalpic contribution or enthalpic situation of 1P in the system. As shown below, we determine H_{1P}^E as a function of mole fraction of 1P, x_{1P}, in the mixed solvent of H_2O + cosolute accurately and in small increments in x_{1P}. We therefore are able to take one more composition derivative graphically without resorting to a fitting function. Thus, we obtain the quantity H_{1P-1P}^E as

$$H_{1P-1P}^{\ \ E} \equiv N(\partial H_{1P}^{\ E}/\partial n_{1P}) = (1 - x_{1P})(\partial H_{1P}^{\ E}/\partial x_{1P}) \tag{2}$$

Equation 2 implies that H_{1P-1P}^E signifies the effect of additional 1P on the actual enthalpic situation of existing 1P. Thus, it provides a measure of 1P−1P interaction in terms of H^E. We call H_{1P-1P}^E the enthalpic interaction function. Because of the thermodynamic stability criterion, the sign of H_{1P-1P}^E indicates whether the 1P−1P interaction is favorable (negative) or unfavorable (positive). The entropy and volume analogues S_{1P-1P}^E and V_{1P-1P}^E have the same meanings in terms of entropy and volume, respectively. However, the favorable/unfavorable propensity is associated with the opposite sign for S_{1P-1P}^E. There is no stability criterion for V_{1P-1P}^E. We stress that the enthalpic interaction, H_{1P-1P}^E, and its entropy and volume analogues are obtained purely experimentally and completely model-free. We might add in passing that the interaction between 1P and the third component could be evaluated similarly as, $H_{1P-3}^E \equiv N(\partial H_{1P}^E/\partial n_3)$, as long as data are available in small enough increments in n_3.

Figure 1 shows the plots of H_{1P-1P}^E in binary 1P−H_2O at 25 °C. 1P works as a typical hydrophobic solute with a medium strength.[6−8,18,19] The x_{1P} dependence of H_{1P-1P}^E together with information from other third derivative quantities led us to suggest[6−8] that the transition of the mixing scheme takes place in a narrow composition range from point *X* (the top of the peak) to *Y* (the right bottom of the peak) in the figure. Point *M* is the median. In the H_2O-rich region below point *X* in the x_{1P}-scale, what we call mixing scheme I is operative, in which 1P enhances the hydrogen bond network of H_2O in its immediate vicinity (i.e., "iceberg formation") and reduces concomitantly the hydrogen bond probability of bulk H_2O away from 1P. Point *X* marks the bond percolation threshold of the hydrogen bond network of bulk H_2O, and the solvent system starts to lose one of the special characteristics of liquid H_2O, the bond-percolated hydrogen bonds. At point *Y*, the transition ends and mixing scheme II sets in, in which the system consists of two kinds of clusters, one rich in H_2O and the other in 1P. Thus, the bond-percolated hydrogen bond network is no longer present.

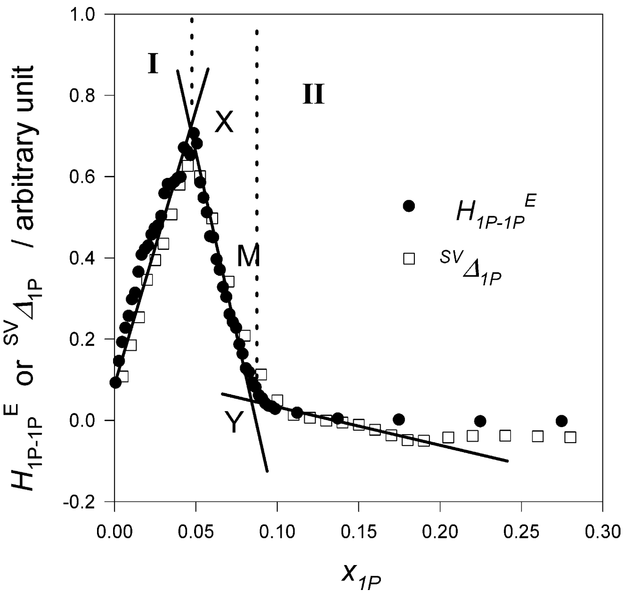

Figure 1. Enthalpic interaction, H_{1P-1P}^E, and partial molar entropy−volume cross fluctuation, $^{SV}\Delta_{1P}$, for binary 1-propanol (1P) − H_2O at 25 °C.

Also shown in Figure 1 are the plots of the partial molar entropy−volume cross fluctuation, $^{SV}\Delta_{1P}$, another third derivative of *G*. $^{SV}\Delta$ is the normalized entropy−volume cross fluctuation defined by us[20−24] earlier as

$$^{SV}\Delta \equiv \langle(\Delta S/\langle V\rangle)(\Delta V/\langle V\rangle)\rangle = RT\alpha_p/V_m \tag{3}$$

where ΔS and ΔV are the local variations in *S* and *V*, α_p the thermal expansivity and V_m the molar volume of the system. $\langle\ \rangle$ signifies the average. We argued that $^{SV}\Delta$ contains qualitative information about the intensity (amplitude) and the extensity (wavelength) of the entropy−volume cross fluctuation.[23,24] Unlike normal liquids, H_2O has a negative contribution to $^{SV}\Delta$ due to the putative presence of icelike patches. Hence the x_{1P} dependence of $^{SV}\Delta$ contains information about the process of changes in water-likeness as 1P is added. Its partial molar quantity, $^{SV}\Delta_{1P}$, is obtained as

$$^{SV}\Delta_{1P} \equiv N(\partial^{SV}\Delta/\partial n_{1P}) = (1 - x_{1P})(\partial^{SV}\Delta/\partial x_{1P}) \tag{4}$$

Hence the behavior of $^{SV}\Delta_{1P}$, another third derivative, shows the effect of 1P on the changes of the water-likeness in terms of $^{SV}\Delta$ as 1P is added. As seen in Figure 1, the fact that the x_{1P} dependence of $^{SV}\Delta_{1P}$ and that of H_{1P-1P}^E match exactly on scaling the ordinate is striking. This indicates that the enthalpic

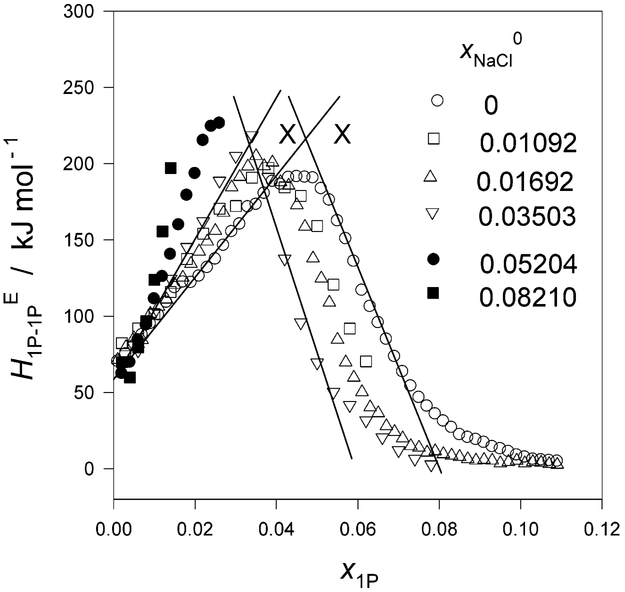

Figure 2. Enthalpic interaction, H_{1P-1P}^{E}, for ternary 1P−NaCl−H$_2$O at 25 °C. x_{NaCl}^{0} is the initial mole fraction of NaCl. Filled symbols signify new data.

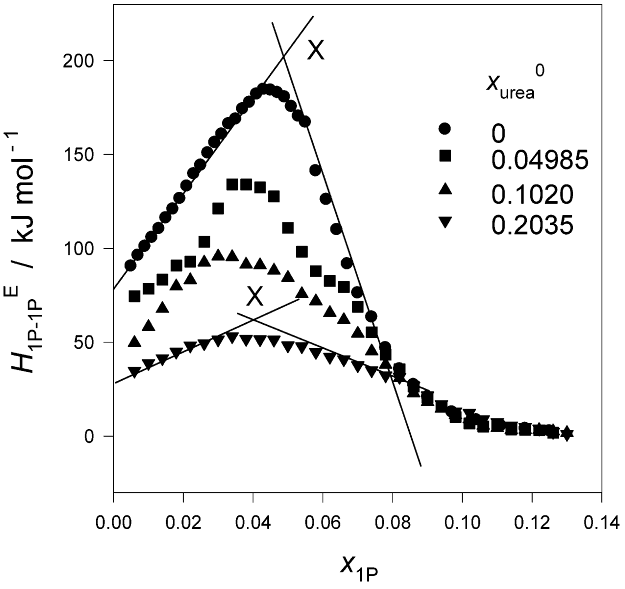

Figure 3. Enthalpic interaction, H_{1P-1P}^{E}, for 1P−urea−H$_2$O at 25 °C. x_{urea}^{0} is the initial mole fraction of urea.

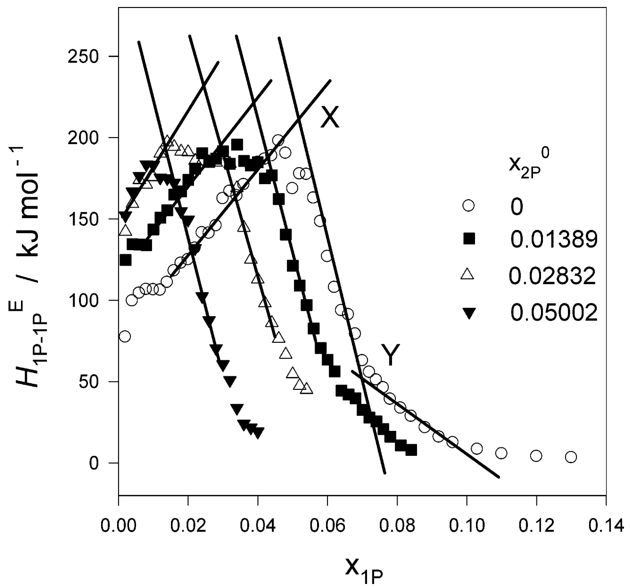

Figure 4. Enthalpic interaction, H_{1P-1P}^{E}, for 1P−2-propanol (2P)−H$_2$O at 25 °C. x_{2P}^{0} is the initial mole fraction of 2P.

1P−1P interaction and the effect of 1P on the entropy−volume cross fluctuation of bulk H$_2$O share the same cause. We concluded therefore that the 1P−1P interaction is H$_2$O-mediated.[23,24] Thus, the x_{1P} dependence of H_{1P-1P}^{E} shows the process of how 1P modifies the nature of H$_2$O in the H$_2$O-rich region. Our present strategy is to monitor the changes in the x_{1P} dependence of H_{1P-1P}^{E} induced by the addition of a cosolute, and to use the resulting changes to learn about the effect of the third component on the molecular organization of H$_2$O.

Figure 2 shows the plots of H_{1P-1P}^{E} in 1P−NaCl−H$_2$O[13] and Figure 3 for 1P−urea−H$_2$O.[12] From the changes induced by addition of NaCl, Figure 2, we suggested that NaCl makes about 7.5 molecules of H$_2$O unavailable for interaction with 1P, perhaps by strongly binding them (hydration), while the remaining bulk H$_2$O stays almost in the same state as in pure H$_2$O. A more detailed discussion on this is given below. A first principle simulation study suggested that the hydration shell of Na$^+$ contains 5.2 molecules of H$_2$O with no effect on H$_2$O molecules beyond the first hydration shell.[25] Figure 3 indicates the effect of urea is qualitatively different. From the fact that the value of H_{1P-1P}^{E} at point *X* decreases while that of x_{1P} remain almost the same, we concluded that urea does not change the hydrogen bond connectivity of H$_2$O by participating in forming the hydrogen bond network of H$_2$O, but at the same time reduces the degree of fluctuation. This conclusion is consistent with suggestion made by a simulation work.[26] Figure 4 shows the equivalent plots for 1P−2-propanol(2P)−H$_2$O.[9] From the previous studies on binary aqueous alcohols, we know that 2P modifies H$_2$O in the same manner as 1P due to its hydrophobicity with almost the same degree.[6−8,18,19] In the ternary 1P−2P−H$_2$O, Figure 4 suggests that 1P and 2P modifies H$_2$O in an additive manner. Namely, 1P works on H$_2$O for the rest of the way to point *X* from where 2P has left off. As a result, the x_{1P} dependence of H_{1P-1P}^{E} is shifted parallel to a progressively smaller value of x_{1P}, without changing the value of H_{1P-1P}^{E}.

Here we apply the same methodology for Na$_2$SO$_4$, NaOOCCH$_3$ (abbreviated as NaOAc), NaClO$_4$, and NaSCN. SO$_4^{2-}$ and SCN$^-$ are at or near the opposite extremes of the Hofmeister series. ClO$_4^-$ is closer to SCN$^-$ despite its size being closer to SO$_4^{2-}$, while Cl$^-$ is in the middle of the above four.

Experimental Section

Na$_2$SO$_4$ (AnalaR, Analytical Reagent, BDH), NaSCN (AnalaR, Analytical Reagent, BDH), NaClO$_4$ (Fluka, Certified ACS >98.0% Crystal, or Aldrich, 98%), NaOOCCH$_3$ (Fisher, Certified ACS Crystal), and NaCl (Fisher, Certified ACS Crystal) 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%, or Fluka, >99.8%(GC)) as supplied was treated in a dry nitrogen atmosphere.

The excess partial molar enthalpies of 1P, H_{1P}^{E}, for cosolute of Na$_2$SO$_4$, NaOAc, NaSCN, and NaCl were determined by a homemade titration calorimeter of a similar design to an LKB Bromma 8700.[17] The uncertainty is estimated as ±0.03 kJ mol^{-1}. For NaClO$_4$, a TAM-2277 titration calorimeter was used. The uncertainty is ±0.003 kJ mol^{-1}, except for the first few points, which give systematically smaller absolute values. The density was measured by a glass pycnometer with the precision

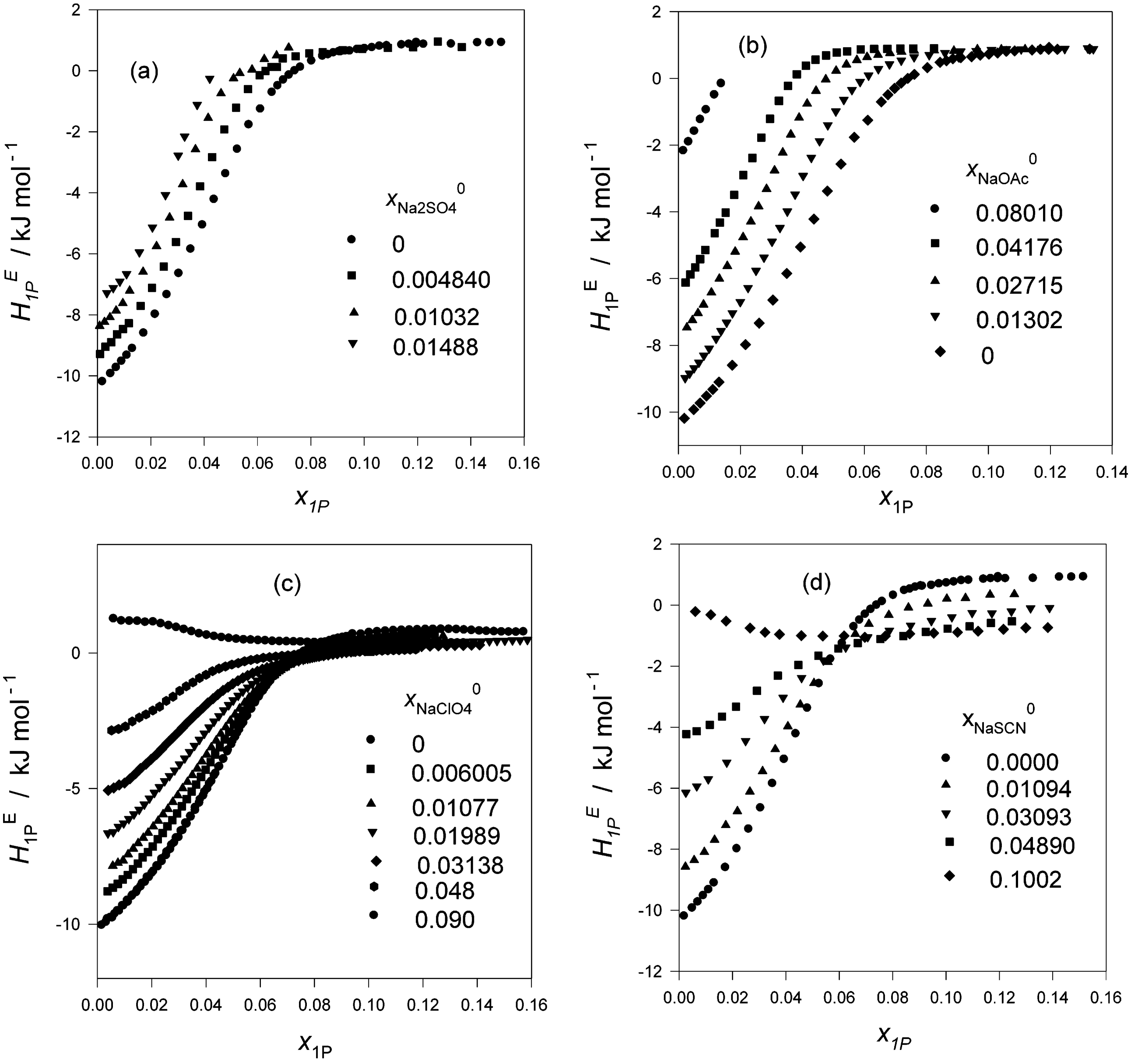

Figure 5. Excess partial molar enthalpy of 1P, H_{1P}^{E}, in 1P−salt−H_2O at 25 °C. x_{salt}^{0} is the initial mole fraction of salt. Salts used are (a) Na_2SO_4, (b) NaOAc, (c) $NaClO_4$, and (d) NaSCN.

± 0.00001 g cm^{-3}. The liquid−liquid-phase separations were determined by turbidity titration. The temperature for all the experiments was controlled to at worst 25.00 ± 0.01 °C.

Results and Discussion

Parts a−d of Figure 5 show the data of H_{1P}^{E} for a given initial mole fraction of each salt. The raw H_{1P}^{E} data are available from the corresponding author. It is immediately apparent that the change induced by addition of salt is qualitatively different between Na_2SO_4 (Figure 5a) and NaSCN (Figure 5d), both being at either ends of the Hofmeister scale. While the effect of Na_2SO_4 is similar to that of NaCl,[13] for NaSCN its effect resembles that of urea.[12] The trend for these and other salts is more clearly seen in H_{1P-1P}^{E}, which is plotted in Figure 6, parts a−d. Together with Figure 2 for NaCl, these graphs provide some clues as to the effect of individual salt on H_2O. To start, we reiterate here the effect of NaCl.[13] In addition to previous data,[13] we obtained H_{1P-1P}^{E} data for high initial NaCl mole fraction, x_{NaCl}^{0}. As x_{NaCl}^{0} increases, point *X*, the point where the bond percolation nature of the hydrogen bond network starts to diminish, occurs at progressively smaller values of x_{1P}. The values of H_{1P-1P}^{E}, on the other hand, remains almost the same at the start, $x_{1P} = 0$, and at point *X*. From these facts, we suggested that a Na$^+$ and Cl$^-$ ion pair hydrates a progressively larger number of H_2O molecules and make them unavailable for 1P to interact to drive the system to point *X*. These loci are plotted in Figure 7 together with phase boundaries.[13] (In the original mixing scheme diagram in ref 13 the median points *M* were shown. The locus of point *Y*, and hence *M* also, is more ambiguous than point *X*. Therefore, we use here the loci of *X*). To their left is the region for mixing scheme I and to the right beyond point *Y* (which is not shown) is for mixing scheme II. The loci of point *X* in Figure 7 seem to form a straight line with the x_{NaCl}^{0} intercept at about 0.12. This indicates that a Na$^+$ and Cl$^-$ ion pair hydrates about 7.5 molecules of H_2O and makes them unavailable for interaction with 1P. From the fact that the values of H_{1P-1P}^{E} at the start, $x_{1P} = 0$, and at point *X* are unaltered on addition of NaCl, it was suggested that the bulk H_2O away from the hydrated ions remains the same as in pure H_2O.[13] Additional data for $x_{NaCl}^{0} = 0.05$ and 0.08 in Figure 2

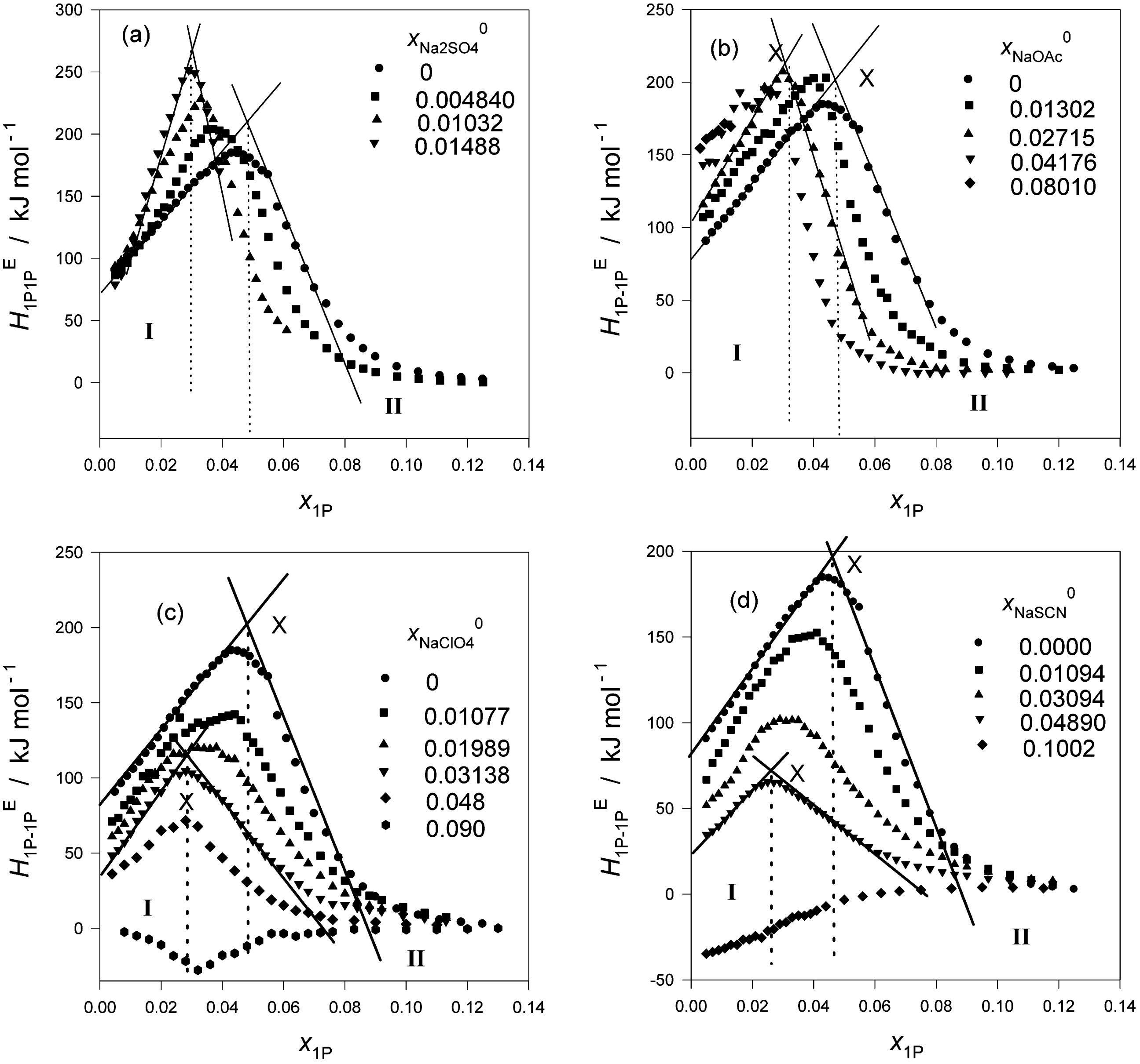

Figure 6. Enthalpic interaction, H_{1P-1P}^E, for 1P–salt–H_2O at 25 °C. x_{salt}^0 is the initial mole fraction of salt. Salts used are (a) Na_2SO_4, (b) NaOAc, (c) $NaClO_4$, and (d) NaSCN.

indicate that the value of H_{1P-1P}^E for these high x_{NaCl}^0 cases also start at about the same value at $x_{1P} = 0$, and increase more sharply pointing toward possible X point at smaller values of x_{1P}. At these high x_{NaCl}^0 composition, the region of single liquid phase is narrow, Figure 7, and the measurements of H_{1P}^E becomes progressively difficult due to slow dissolution of 1P. Hence it was impossible to locate point X. For $x_{NaCl}^0 = 0.05$, however, the last point in Figure 2 may be close to point X, which is also shown by a hollow square symbol in Figure 7. Nonetheless, H_{1P-1P}^E seems to behave in the same manner as for lower x_{NaCl}^0 cases. This suggests that the mixing scheme 1 remains operative up to precipitation of NaCl at $x_{NaCl}^0 = 0.1$. Namely, the bulk H_2O away from the hydration shell remains unperturbed up to saturation.

Na_2SO_4 seems to have a similar effect on H_2O to NaCl, Figure 6a, except that the values of H_{1P-1P}^E at point X increase as $x_{Na_2SO_4}^0$ increases. However, the facts that the value of H_{1P-1P}^E remains almost constant at $x_{1P} = 0$ and the loci of point X shift toward smaller values of x_{1P} may hint Na_2SO_4 also hydrates a number of H_2O molecules and makes them unavailable for 1P, with some additional effect of raising the value of H_{1P-1P}^E at point X. The loci of point X are shown in Figure 8a, which forms a straight line with the intercept at $x_{Na_2SO_4}^0 = 0.037$. This suggests that two Na^+ and a SO_4^{2-} ions hydrate 26 H_2O molecules, if Na_2SO_4 indeed hydrates. Recent photoemission[27] and simulation[28] studies indicate 12–16 molecules of H_2O are bound to SO_4^{2-}. If the hydration number for Na^+ is 5.2,[25] the total number of hydration for Na_2SO_4 matches our observation. At point X, however, the enthalpic interaction between 1P-(iceberg-clad) molecules is stronger in Na_2SO_4 solution than in pure H_2O or aqueous NaCl. This means that the effect of 1P on the $S-V$ cross fluctuation, ${}^{SV}\Delta_{1P}$, is higher at point X than in pure H_2O. Or the negative contribution to ${}^{SV}\Delta_{1P}$, the degree of H_2O-likeness, diminishes more strongly in the presence of Na_2SO_4 than in pure H_2O or NaCl aqueous solution. These could be a reflection of interaction between 1P and Na_2SO_4 in aqueous solution. As a result 1P-rich phase separates out (i.e., the salting out effect) at smaller values of $x_{Na_2SO_4}^0$ and x_{1P} than for NaCl.

Figure 6b shows that NaOAc affects H_2O in a different manner from NaCl and Na_2SO_4. Its effect on the x_{1P} dependence of H_{1P-1P}^E is basically similar to that of 2-propanol, Figure 4. However, the initial increase of H_{1P-1P}^E before point X is not

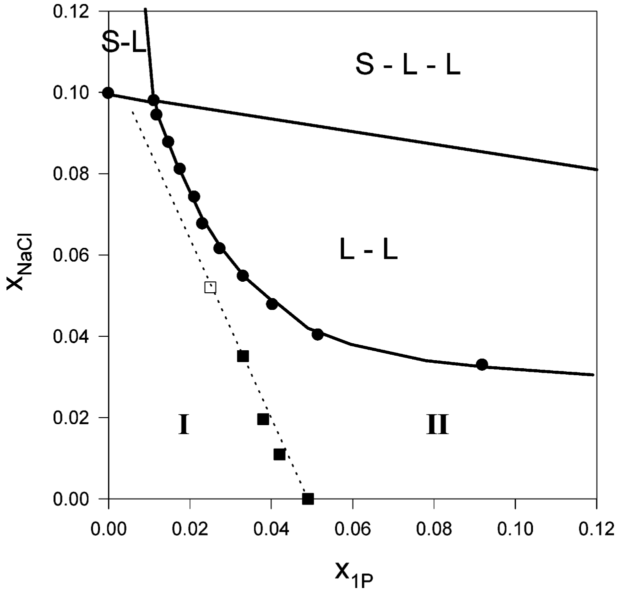

Figure 7. Phase and mixing scheme diagram for 1P−NaCl−H_2O at 25 °C.

parallel as the case for 2P, Figure 4, but is progressively sharper. This is due to contribution from Na^+ ion, as in NaCl case. We suggest, therefore, that OAc^- modifies the molecular organization of H_2O in a similar manner as alcohol. If so, then in binary NaOAc−H_2O there must be a transition to mixing scheme II, as is typical for aqueous solution of an hydrophobic solute.[7,8] Whether this occurs below saturation, $x_{NaOAc}^0 = 0.09989$ is yet to be determined. However, dissolution of 1P into NaOAc−H_2O in these higher concentration of x_{NaOAc}^0 is extremely slow, on the order of hours, and hence a better adiabatic shield may have to be installed surrounding the calorimeter cell before this issue could be settled. At this point, the mixing scheme boundary could be either of case A or B, shown in Figure 8b. Regarding the shift of point X toward smaller values of x_{1P} as x_{NaOAc}^0 increases, this is caused by a different mechanism from NaCl and possibly Na_2SO_4 cases. It is therefore dangerous to estimate the number of hydrated H_2O, in the manner used for the latter two salts.

Parts c and d of Figure 6 are for $NaClO_4$ and NaSCN. It is clear that both anions modify the molecular organization of H_2O in a similar manner as urea, Figure 3, except that a shift of point X to smaller values of x_{1P} is evident. This must be from contribution at least in part by Na^+ ions. The main effect is direct interactions of ClO_4^- and SCN^- ions with the hydrogen bond network of H_2O, keeping the hydrogen bond connectivity but retarding the degree of fluctuation inherent in liquid H_2O. This is operative up to about 0.05 in the mole fraction of these salts, beyond which the x_{1P} dependence of H_{1P-1P}^E changes dramatically, as seen in Figure 6c and 6d. This hints that there are mixing scheme II in binary $NaClO_4$−H_2O, and NaSCN−H_2O systems. The transition point could be between the mole fraction 0.05 and 0.1. These are shown in Figure 8c.

Within these five salts we have studied, each salt modifies H_2O in its own qualitatively unique way, except for $NaClO_4$ and NaSCN whose effects are similar to each other, but qualitatively different from the other three. In terms of partial molar volume of 1P in these salt solutions shown in Figure 9, the qualitatively unique effect of each salt is evident also. However, the data points are not sufficient to warrant graphical differentiation to evaluate the volumetric interaction, $V_{1P-1P}^E = N(\partial V_{1P}^E/\partial n_{1P})$. Further discussion using volume data is therefore postponed.

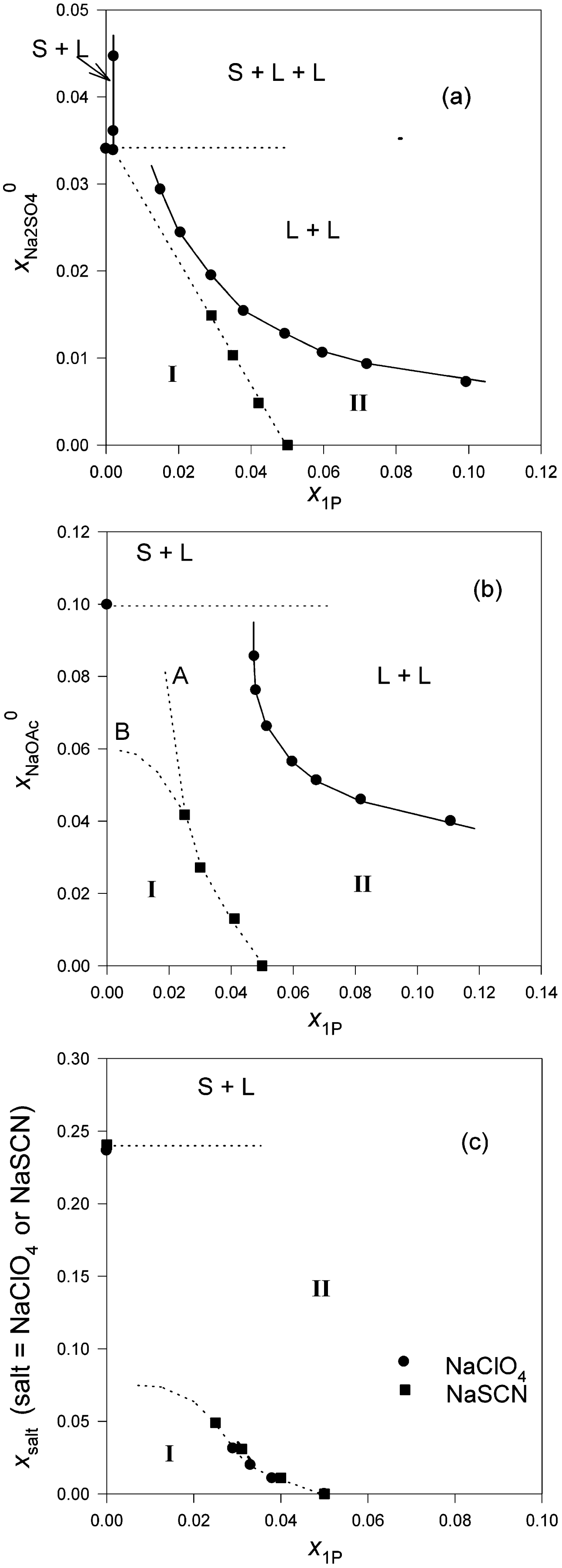

Figure 8. Phase and mixing scheme diagram for 1P−salt−H_2O at 25 °C. Salts used are (a) Na_2SO_4, (b) NaOAc, (c) $NaClO_4$ (filled circle), and NaSCN (filled square).

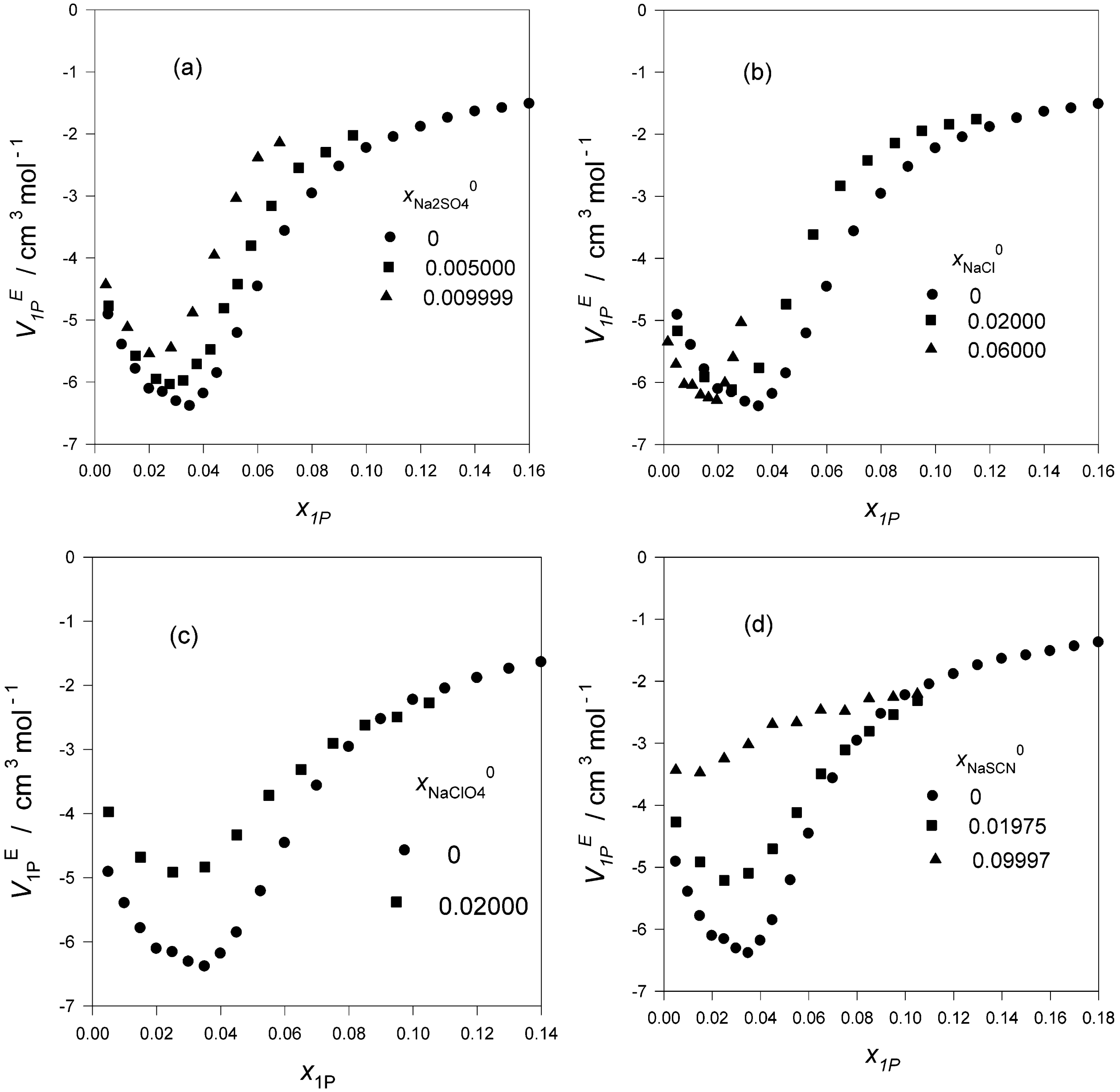

Figure 9. Excess partial molar volume of 1P in 1P−salt−H_2O at 25 °C. x_{salt}^0 indicates the initial mole fraction of salt. Salts used are (a) Na_2SO_4, (b) NaCl, (c) $NaClO_4$, and (d) NaSCN.

To seek more quantitative interpretation of the effect of each salt on H_2O in relation to the order of the Hofmeister series, we plot various attributes of the x_{1P} dependence of H_{1P-1P}^{E}, Figure 6. Parts a−c of Figure 10 show the traces of x_{1P} and H_{1P-1P}^{E} values of point *X* and the value of H_{1P-1P}^{E} at $x_{1P} = 0$ as the salt concentration increases. Figure 10a is the collection of the locus of x_{1P} at point *X* shown in Figure 8. Also indicated with a solid line on the abscissa is the saturation mole fraction of the respective binary aqueous solutions. For $NaClO_4$ and NaSCN, they are off the scale, at 0.2367 and 0.2406, respectively. The dotted line indicates probable boundary from mixing scheme I to II for these latter two salts. While such boundary evidently exists between 0.05 and 0.09 of the salt mole fraction (see Figure 6, parts c and d), its precise location is yet to be determined by a detailed study on the binary aqueous solution of these salts. For NaOAc, the existence of the transition of mixing scheme should be expected just as with a hydrophobic solute.[6−8] However, whether this occurs below the saturation $x_{\mathrm{NaOAc}}^0 = 0.09982$ remains to be seen by a detailed study also on binary NaOAc−H_2O. As discussed above, if hydration is the only effect of salts on H_2O, the slope of Figure 10a, or its x_{salt} intercept gives the hydration number. Thus, NaCl hydrates about 8 and Na_2SO_4 26 H_2O molecules. The mechanisms for negative slopes in Figure 10a for other salts are not hydration. NaOAc acts partially as hydrophobic as alcohols, while $NaClO_4$ and NaSCN are hydrophilic as urea. For the latter three salts, Na^+ ion must be hydrating some H_2O molecules as in NaCl and negative slopes in the figure may be partly due to this effect. However, their loci (more clearly seen in Figure 8, parts b and c) seem to form a curve and separation of the effect of Na^+ is not immediately possible. Figure 10b shows that the values of H_{1P-1P}^{E} at point *X* for NaOAc and NaCl remain almost constant on addition of salt. This apparently same behavior is, however, coming from completely different mechanisms, which is apparent in Figure 10c in that the value of H_{1P-1P}^{E} at $x_{1P} = 0$ increases for NaOAc while that for NaCl remains almost constant. That H_{1P-1P}^{E} at point *X* decreases at the same rate for $NaClO_4$ and NaSCN is coming from the same mechanism; ClO_4^- and SCN^- connect directly to the hydrogen bond network

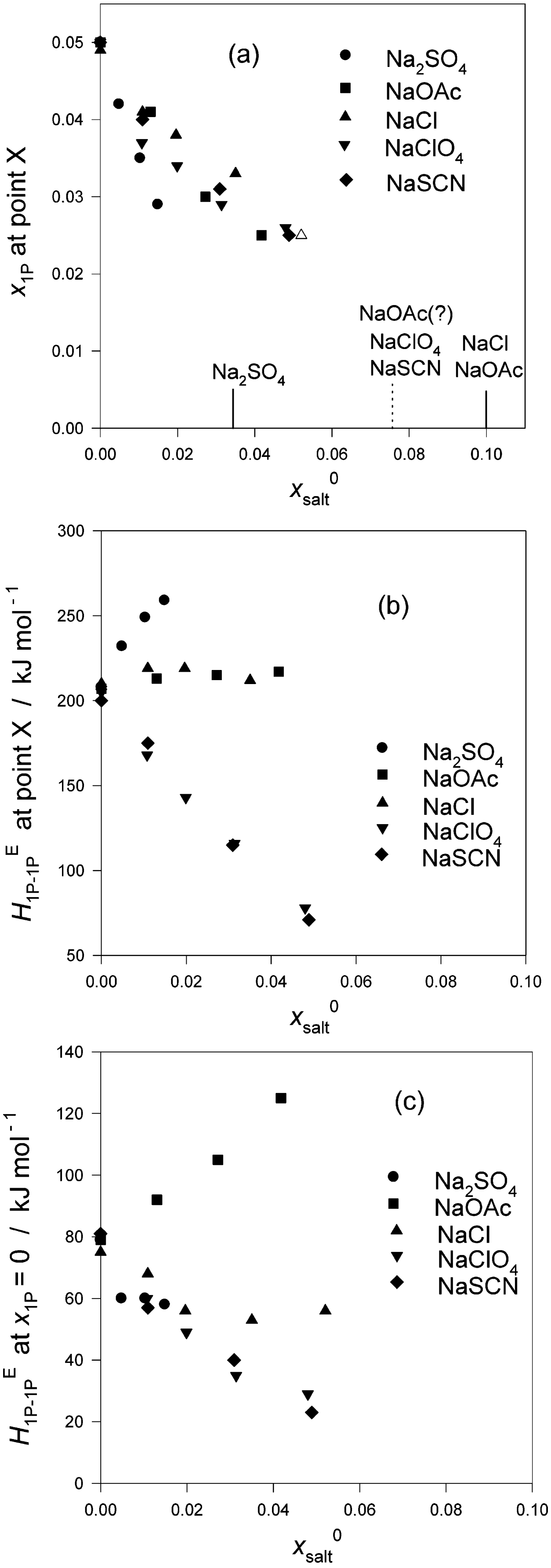

Figure 10. (a) Locus of point X in terms of x_{1P} for 1P−salt−H_2O at 25 °C. (b) Value of H_{1P-1P}^{E} for 1P−salt−H_2O at 25 °C. (c) Value of H_{1P-1P}^{E} at $x_{1P} = 0$ for 1P−salt−H_2O at 25 °C.

of H_2O and reduce the degree of fluctuation inherent in liquid H_2O.

Conclusions

Within the present work, in which five anions with the countercation fixed with Na^+ were studied, each salt has its own unique, qualitatively different manner of modifying the molecular organization of H_2O. It is clear, however, that the integrity as liquid H_2O is partially retained in the water-rich region. The integrity of H_2O may be described briefly as having the bond percolated hydrogen bond network and having also unusually large degree of fluctuation, in terms of intensity (amplitude) as well as extensity (wavelength). Each salt modifies a part or parts of the characteristics of H_2O. NaCl hydrates about eight H_2O molecules but leaves the bulk H_2O beyond the hydration shell unaltered. Thus, NaCl simply works by retarding the quantitative availability of H_2O toward an additional solute including biopolymers. Na_2SO_4 also hydrates about 26 H_2O molecules, but at the same time it increases the entropy−volume cross fluctuation or reduces its negative part (i.e., water likeness) of the bulk H_2O. NaOAc aside from the hydration effect by Na^+ ion, OAc^- modifies H_2O similar to alcohols, which are known to act as hydrophobic solutes.[6−8] Namely, this anion enhances the hydrogen bond network of H_2O in its immediate vicinity, with concomitant reduction of the hydrogen bond probability of H_2O in the bulk away from OAc^-. ClO_4^- and SCN^- ions, on the other hand, connect to the hydrogen bond network of H_2O and keep the hydrogen bond connectivity intact as with urea.[12] At the same time, they reduce the degree of fluctuation of H_2O by breaking the H donor/acceptor symmetry of H_2O's hydrogen bond network. The strength of such effect seems similar between these two anions. More subtle difference may have to be sought in the way each reduces the fluctuation in H_2O, before direct connection to the Hofmeister ranking of $ClO_4^- > SCN^-$ can be made.

While Na^+ seems to hydrate a number less than seven H_2O molecules and to leave the bulk H_2O unperturbed, it seems dangerous to generalize the present observation for the five anions in relation to the Hofmeister ranking. It seems reasonable to state, however, that the effect of each salt is complex and qualitatively different, and the net phenomenological result as manifested as the Hofmeister series is due to the holistic effect of many factors. Hence, a single parameter or a small number of parameters of the salt solutions may not be able to account for the Hofmeister effect, as a large number of studies have already experienced. In any case, further well organized studies seem mandatory.

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Supporting Information Available: Table 1S containing the loci of phase boundaries and mixing scheme boundaries shown in Figure 8, and Table 2S containing the raw density data from which V_{1P}^{E} values shown in Figure 9 were calculated. This information is available free of charge via the Internet at http://pubs.acs.org.

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