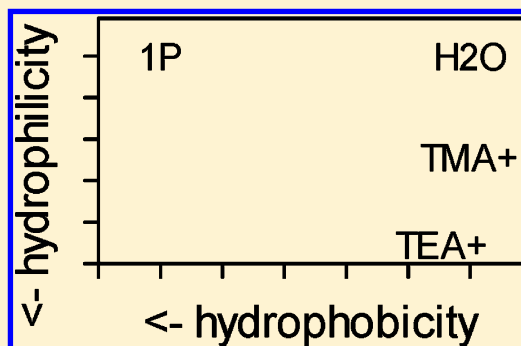


Effects of Tetramethyl- and Tetraethylammonium Chloride on H<sub>2</sub>O: Calorimetric and Near-Infrared Spectroscopic StudyYoshikata Koga,<sup>\*,†</sup> Fumie Sebe,<sup>‡,§</sup> and Keiko Nishikawa<sup>‡</sup><sup>†</sup>Suitekijuku (Water Drop Institute), Vancouver, BC, Canada V6R 2P5, and Department of Chemistry, The University of British Columbia, Vancouver, BC, Canada V6T 1Z1<sup>‡</sup>Graduate School of Advanced Integration Sciences, Chiba University, Chiba 263-8522 Japan

## S Supporting Information

**ABSTRACT:** The effect of tetraethylammonium chloride (TEAC) on H<sub>2</sub>O was investigated by the 1-propanol (1P) probing thermodynamic methodology developed by us earlier. It was found that TEAC is an amphiphile with a small hydrophobic and a dominant hydrophilic contribution. An earlier application of the same 1P-probing methodology to tetramethylammonium chloride (TMAC) indicated that the latter is as hydrophilic as urea without any hydrophobic contribution. The hydrophilic effect of TEAC was found to be about twice stronger than that of TMAC. To investigate further these surprising findings, we applied a new analysis method using the concept of the excess partial molar absorptivity of the solute on the  $\nu_2 + \nu_3$  combination band of H<sub>2</sub>O in the near-infrared (NIR) range of their aqueous solutions. The results confirmed that both salts are indeed strongly hydrophilic toward H<sub>2</sub>O which manifests itself in the 5123 cm<sup>-1</sup> chromophore of the NIR band of H<sub>2</sub>O. Furthermore, we suggest from the behavior of the 5263 cm<sup>-1</sup> band that both solutes might form small aggregates in the H<sub>2</sub>O-rich region of the respective aqueous solutions.



## ■ INTRODUCTION

Regarding the effects of tetraalkylammonium cations (RN<sub>4</sub><sup>+</sup>) on H<sub>2</sub>O, a large number of investigations have been carried out and the proposed conclusions are confusing and controversial. The majority of investigations regarded R<sub>4</sub>N<sup>+</sup> ions as typical hydrophobic solutes, presumably because of the presence of four alkyl groups, and concluded that they increase the relative population of more ordered hydrogen bondings in the vicinity of solute.<sup>1–8</sup> Some argued that there are hydration shells like clathrates around RN<sub>4</sub><sup>+</sup> but emphasized that H<sub>2</sub>O in hydration shells are not at all different from those in pure H<sub>2</sub>O.<sup>5–8</sup> Others noted a qualitative difference between those with smaller (R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>) and larger alkyl moieties, the latter being hydrophobes and the former hydrophiles.<sup>9–12</sup> Yet a few other investigations conclude that none of the R<sub>4</sub>N<sup>+</sup> homologues are hydrophobic.<sup>13,14</sup>

Hydrophobicity/hydrophilicity distinction has been a loose concept based on human experiences. Thermodynamically, the hydration free energy is often used as a one-dimensional scale.<sup>15,16</sup> While free energy  $G$  dictates the fate of an equilibrium system, more detailed information can be obtained from its derivative quantities with respect to the independent variables ( $p$ ,  $T$ ,  $n_i$ ), where  $n_i$  is the molar amount of the  $i$ th component. The higher the order of the derivative, the more clearly subtleties in intermolecular interactions would stand out.<sup>17</sup> We pursued this principle and studied aqueous solutions of electrolytes and nonelectrolytes using the second and the

third derivative quantities.<sup>18–20</sup> In particular, we defined and determined the enthalpic solute–solute interaction  $H_{SS}^E$  as<sup>18–20</sup>

$$\begin{aligned} H_{SS}^E &\equiv N(\partial H_S^E / \partial n_S) \\ &= N(\partial^2 H^E / \partial n_S^2) \\ &= (1 - x_S)(\partial H_S^E / \partial x_S) \end{aligned} \quad (1)$$

where  $H_S^E$  is the excess partial molar enthalpy of solute  $S$  in the binary  $S$ –H<sub>2</sub>O system.  $H^E$  and  $n_S$  are the total excess enthalpy of the system and the molar amount of solute  $S$ , respectively, together with the molar amount of H<sub>2</sub>O,  $n_W$ ,  $N = n_S + n_W$  and  $x_S = n_S/N$ . Since  $H_S^E \equiv (\partial H_S^E / \partial n_S)$  is the second derivative of  $G$  with respect to  $T$  and  $n_S$ ,  $H_{SS}^E$  is the third derivative. As is explained in Appendix A in the Supporting Information, the  $x_S$  dependence pattern of  $H_{SS}^E$  distinguishes particularly clearly hydrophobes from hydrophiles and vice versa. In turn, we propose to classify hydrophobes/hydrophiles/amphiphiles by the  $x_S$  dependence pattern of  $H_{SS}^E$ , as detailed in Appendix A.

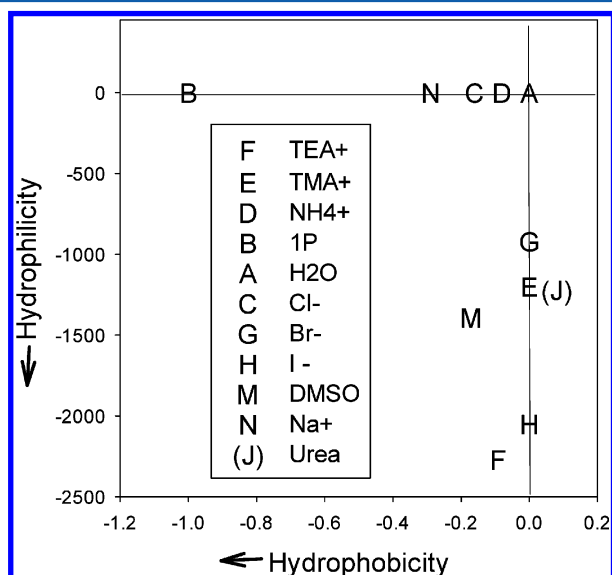
Furthermore, we devised what we call the 1-propanol (1P) probing methodology based on our findings on a variety of binary  $S$ –H<sub>2</sub>O.<sup>21,22</sup> A brief account is given in Appendix B in the Supporting Information. This approach provides additional information about hydrophobicity/hydrophilicity/amphiphilic-

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ity in that the effect of S on H<sub>2</sub>O is displayed on a two-dimensional map. Hence, a subtle difference among amphiphiles, a relative strength of hydrophobic and hydrophilic contributions, is clearly distinguishable. We have applied the 1P methodology to a number of solutes, and the resulting hydrophobicity/hydrophilicity indices for selected nonelectrolytes and electrolytes are plotted in Figure 1.



**Figure 1.** Hydrophobicity/hydrophilicity map. TEA<sup>+</sup> (point F in the figure) is the result of the present work. For references to other works, see text.

H<sub>2</sub>O defines the origin, and the probing 1P is at point B (−1,0) on the abscissa. Relative to these points, “hydrophobes” (and “hydration centers”) spread to the west on the abscissa, and “hydrophiles” to the south on the ordinate. Amphiphiles show up in the southwest quadrant of the map. We stress that this 1P probing is applicable only in the H<sub>2</sub>O-rich region, in which the integrity of liquid H<sub>2</sub>O is retained as monitored by the presence of the peak type pattern of  $H_{1P1P}^E$ . Our earlier application of this method on a number of cations indicated that tetramethylammonium ion (TMA<sup>+</sup>) was found at almost the same spot E in Figure 1 as a typical hydrophile, urea (J).<sup>23–26</sup> Namely, within this methodology, TMA<sup>+</sup> is a hydrophile as strong as urea. We suggested that the H in the CH<sub>3</sub> group attached to N atom becomes susceptible to hydrogen bonding with H<sub>2</sub>O in the hydration shell due to a stronger electronegativity of N.<sup>23</sup> We apply the same methodology here to an aqueous solution of tetraethylammonium chloride (TEAC) to see if an extra C atom between N atom and the terminal methyl group weakens the influence of N.

**Excess Partial Molar Absorptivity of Aqueous TMAC and TEAC.** To seek additional information about the classification “hydrophobicity/hydrophilicity” from spectroscopic studies, we have introduced a concept of the excess partial molar absorptivity of solute S in the analysis of the spectra of the  $\nu_2 + \nu_3$  combination band of H<sub>2</sub>O in the near-infrared region, and applied it to aqueous solutions of nonelectrolytes<sup>27</sup> and salts.<sup>28</sup> The  $\nu_2$  is known as the asymmetric stretch and the  $\nu_3$  the bending mode of H<sub>2</sub>O molecule. Following the solution thermodynamics tradition, we first isolate the effect of nonideality due to many-body

interactions in aqueous solution on the molar absorptivity  $\epsilon$  as the excess molar absorptivity,  $\epsilon^E$ , defined as

$$\epsilon = (A/l)(V/N) = x_S \epsilon_S^0 + x_W \epsilon_W^0 + \epsilon^E \quad (2)$$

where  $A$  is the absorbance,  $l$  the path length,  $V$  the volume of sample through which light passes, and  $N$  the total molar amount of solution,  $\epsilon_S^0$  and  $\epsilon_W^0$  are the molar absorptivity of pure S and H<sub>2</sub>O, respectively.

The resulting values of  $\epsilon^E$  evaluated for aqueous acetonitrile, a “hydrophobe”,<sup>29</sup> and acetone, a “hydrophile”,<sup>30</sup> showed distinctive two bands at the same wavenumbers,  $\omega$ : a weakly negative one at 5020 cm<sup>−1</sup> and a strongly positive one at 5230 cm<sup>−1</sup>.<sup>27</sup> Namely, the effect of intermolecular interactions on the  $\nu_2 + \nu_3$  band of H<sub>2</sub>O is isolated into two  $\omega$ -regions; the excess (nonideal) portion of the transition moment is altered negatively at 5000 cm<sup>−1</sup> and in a positive manner at 5200 cm<sup>−1</sup>  $\omega$  regions only. This is an important finding. Following the results by Fornes and Chaussidon,<sup>31</sup> we attributed the chromophore at 5000 cm<sup>−1</sup> to be solidlike H<sub>2</sub>O assembly and that at 5200 cm<sup>−1</sup> liquidlike. When  $\epsilon^E$  values were evaluated for Na halides,<sup>28</sup> we found three distinctive bands: a negative band at 4873 cm<sup>−1</sup>, a positive one at 5123 cm<sup>−1</sup>, and a negative one at 5263 cm<sup>−1</sup>. We interpreted that the negative band due to solidlike H<sub>2</sub>O apparent in aqueous nonelectrolytes red-shifted by 120 cm<sup>−1</sup>, the positive liquidlike band red-shifted by 80 cm<sup>−1</sup>, and a new negative peak appeared at 5263 cm<sup>−1</sup> in aqueous electrolytes. The latter was attributed to free H<sub>2</sub>O molecules without hydrogen bonding under the influence of electric charges of ions.<sup>28</sup>

To see the effect of solute on  $\epsilon^E$  more clearly, we defined and calculated the excess *partial* molar absorptivity of solute,  $\epsilon_S^E$ , as

$$\epsilon_S^E \equiv N(\partial \epsilon^E / \partial n_S) = (1 - x_S)(\partial \epsilon^E / \partial x_S) \quad (3)$$

This quantity,  $\epsilon_S^E$ , is the change in  $\epsilon^E$ , the nonideality of the solution in terms of molar absorptivity of the  $\nu_2 + \nu_3$  band of H<sub>2</sub>O, induced by perturbing the system by an infinitesimal increase in  $n_S$  keeping  $n_W$  constant. The resulting change  $\delta \epsilon^E$  is normalized by  $(\delta n_S / (N + \delta n_S))$ , in the limit of  $\delta n_S \rightarrow 0$ . Such a normalization factor is necessary for  $\epsilon^E$  being an intensive quantity, just as  $H_S^E$  was an intensive quantity in evaluating  $H_{SS}^E$  by eq 1.<sup>32</sup>

In the earlier work,<sup>27</sup> the resulting  $\epsilon_S^E$  for aqueous acetonitrile and acetone indicated that the effect of a hydrophobic acetonitrile is apparent in the solidlike chromophore, while that of a hydrophilic acetone manifests itself in the liquidlike band. Thus, the distinction between a “hydrophobe” and a “hydrophile” learned by the 1P-probing thermodynamic study has additional information from the NIR study.<sup>27</sup> The similar study on aqueous solutions of Na-halides revealed that the qualitative distinction between Cl<sup>−</sup> and (Br<sup>−</sup>, I<sup>−</sup>) pair, the former being a hydration center at point C in Figure 1 but the latter hydrophiles at points G and H, is apparent only in the 5123 cm<sup>−1</sup> liquidlike chromophore.<sup>28</sup>

Here we apply the same analysis for NIR study for aqueous solutions of tetramethyl- and tetraethylammonium chlorides (TMAC and TEAC), to seek additional information about their hydrophobicity/hydrophilicity.

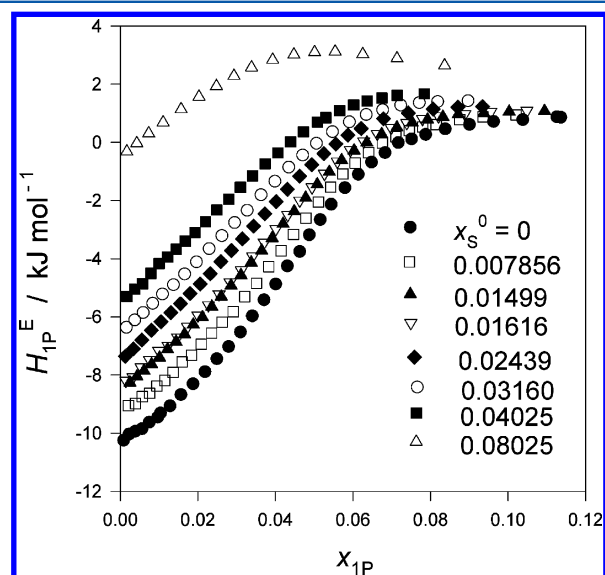
## ■ EXPERIMENTAL SECTION

Tetraethylammonium chloride (J. T. Baker, >98%), 1-propanol (Aldrich, 99.7%), and H<sub>2</sub>O (Anachemia, distilled in glass) were used for the calorimetric study as supplied. For the NIR study,

tetramethyl- and tetraethylammonium chlorides (Wako, >98%) were used as supplied. H<sub>2</sub>O was freshly distilled using Yamato Kagaku Autostill WG201. The calorimeter for determination of  $H_{1P}^E$  was home-built in a similar design to an LKB Bromma 8700 semi-isothermal titration calorimeter. The titration of 1P into the calorimeter cell was carried out in a dry N<sub>2</sub> atmosphere. The temperature of the bath in which the calorimeter is immersed was kept at  $25.000 \pm 0.005$  °C. The uncertainty in  $H_{1P}^E$  is estimated to be better than  $\pm 0.01$  kJ·mol<sup>-1</sup>. An NIR spectrophotometer was also home-constructed as described elsewhere.<sup>33</sup>

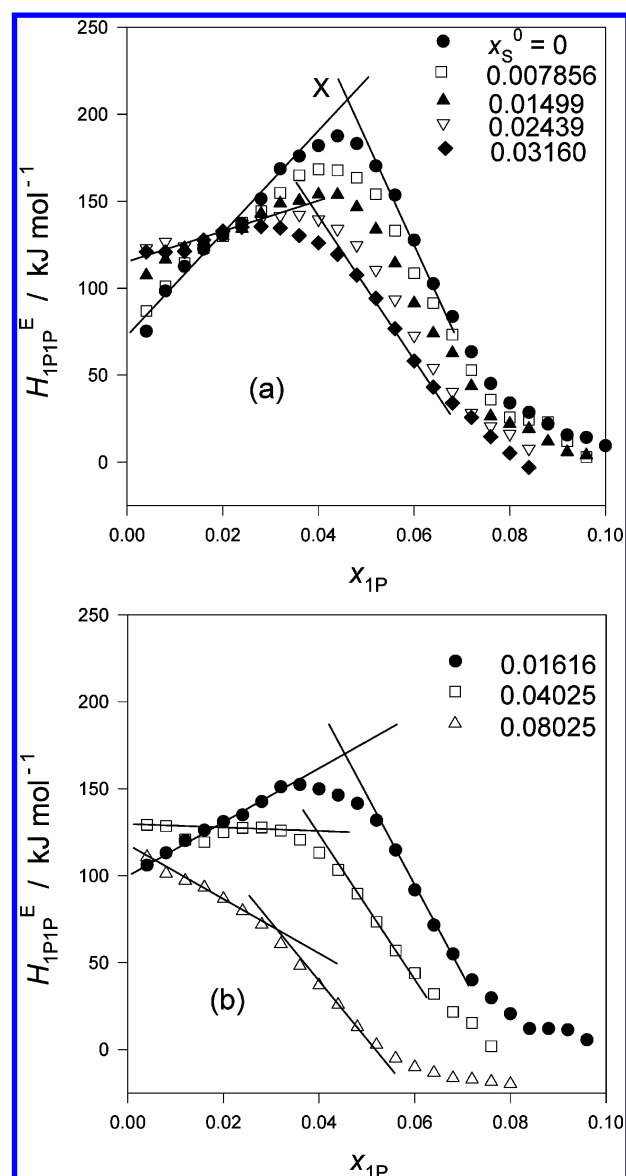
## RESULTS AND DISCUSSION

**Calorimetric Study by 1P-Probing Methodology.** The excess partial molar enthalpies of 1P,  $H_{1P}^E$ , are given in Table S1 in the Supporting Information and are plotted in Figure 2. For



**Figure 2.** Excess partial molar enthalpy of 1-propanol (1P) in 1P–S–H<sub>2</sub>O at 25 °C, for S = tetraethylammonium chloride (TEAC).

$x_S^0 = 0$  (S = TEAC), the  $x_{1P}$  dependence of  $H_{1P}^E$  shows a sigmoid increase with an inflection point at about  $x_{1P} \approx 0.05$ . This behavior is typical for a hydrophobic 1P, and the inflection point becomes a peak top in the next derivative  $H_{1P1P}^E$ . As the third component S is added and  $x_S^0$  increases, this behavior becomes less conspicuous and at  $x_S^0 = 0.08$ ,  $H_{1P}^E$  increases in a convex manner without any inflection point. Figure 3 shows the enthalpic 1P–1P interaction function  $H_{1P1P}^E$  evaluated graphically.<sup>34</sup> As is evident in Figure 3b, for  $x_S^0 \geq 0.04$  the  $x_{1P}$  dependence pattern of  $H_{1P1P}^E$  does not show a peak any more but a break in slope. As discussed above, the 1P-probing methodology is applicable as long as the  $H_{1P1P}^E$  pattern shows a peak type anomaly which assures that the mixed solvent retains the integrity of liquid H<sub>2</sub>O.<sup>35</sup> Thus, we must limit ourselves in the range  $x_S^0 < 0.03$ . As evident in Figure 3b, the  $H_{1P1P}^E$  pattern changed from a peak type to the one showing a break in slope at about  $x_S^0 = 0.04$ . Namely, the  $H_{1P1P}^E$  pattern for  $x_S^0 = 0.04$  and 0.08 shown in Figure 3b is the same type as the  $H_{SS}^E$  pattern for S = dimethyl sulfoxide (DMSO), shown in Figure A1(b) in Appendix A in the Supporting Information. Indeed, the same  $H_{1P1P}^E$  pattern change was observed for the 1P–DMSO–H<sub>2</sub>O ternary system for a recent application of the 1P-probing methodology to study the effect of DMSO on H<sub>2</sub>O.<sup>36</sup> It was

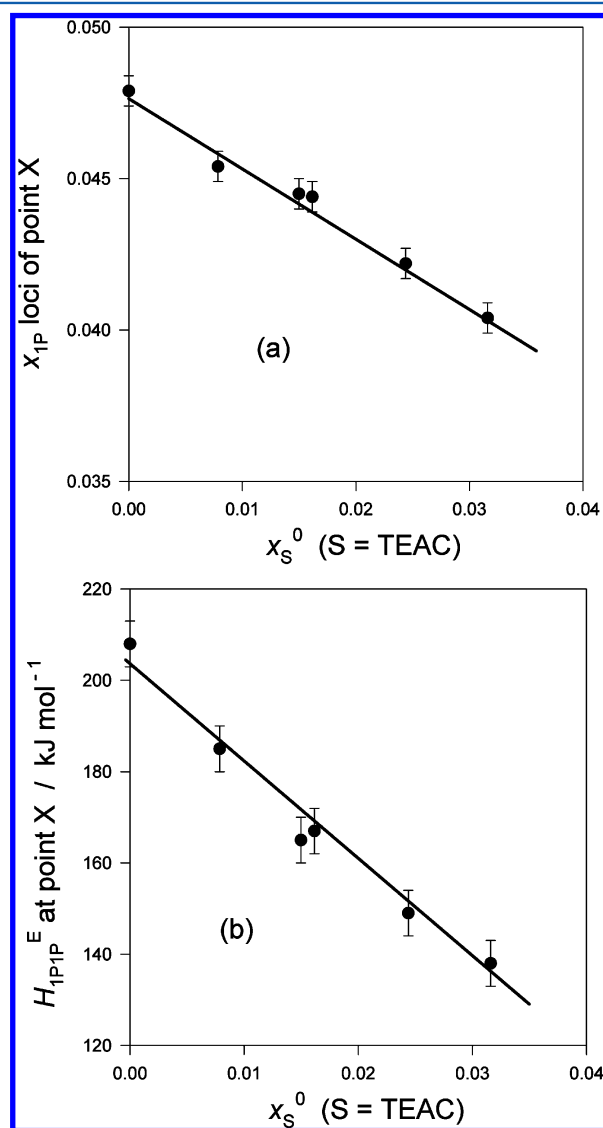


**Figure 3.** (a) 1P–1P enthalpic interaction,  $H_{1P1P}^E$ , in 1P–S–H<sub>2</sub>O at 25 °C for S = TEAC and given initial mole fractions of S,  $x_S^0$ . (b) 1P–1P enthalpic interaction,  $H_{1P1P}^E$ , in 1P–S–H<sub>2</sub>O at 25 °C for S = TEAC and given initial mole fractions of S,  $x_S^0$ .

suggested that DMSO molecules aggregates as a dimer or trimer from the outset in aqueous solution<sup>37</sup> and that in the 1P-probing experiments the probing 1P is trapped in the DMSO aggregates above a certain threshold value of  $x_S^0$  (S = DMSO) and hence  $H_{1P1P}^E$  apparently shows  $H_{SS}^E$  for S = DMSO.<sup>36</sup> Thus, the observation in Figure 3b hints that TEAC molecules also make small aggregates at the outset and the probing 1P begins to be trapped in such aggregates at about  $x_S^0$  (S = TEAC) = 0.04. Thus,  $H_{1P1P}^E$  pattern resembles that of  $H_{SS}^E$  for amphiphile above this threshold,  $x_S^0 = 0.04$ . As the loci for TEA<sup>+</sup>, point F, indicates in Figure 1 that TEA<sup>+</sup> is indeed an amphiphile. This is only a speculation at this point but gains support from the NIR study below. The previous application of the 1P-probing methodology on TMAC indicated such pattern change in  $H_{1P1P}^E$  was not observed and a peak type pattern remained up to  $x_S^0$  (S = TMAC) = 0.08.<sup>26</sup> This does not necessarily mean, however, that TMAC molecules do not form such small aggregates as TEAC. The case could be possible that the probing 1P is not

trapped in possibly small TMAC aggregates up to  $x_S^0$  ( $S = \text{TMAC}$ ) = 0.08, and still TMAC modifies  $\text{H}_2\text{O}$  also as aggregates.

Figure 4 shows the plots of the locus of point X, the top of the peak in Figure 3, against  $x_S^0$ . Both  $x_{\text{IP}}$  and  $H_{\text{IP}}^{\text{E}}$  loci of point

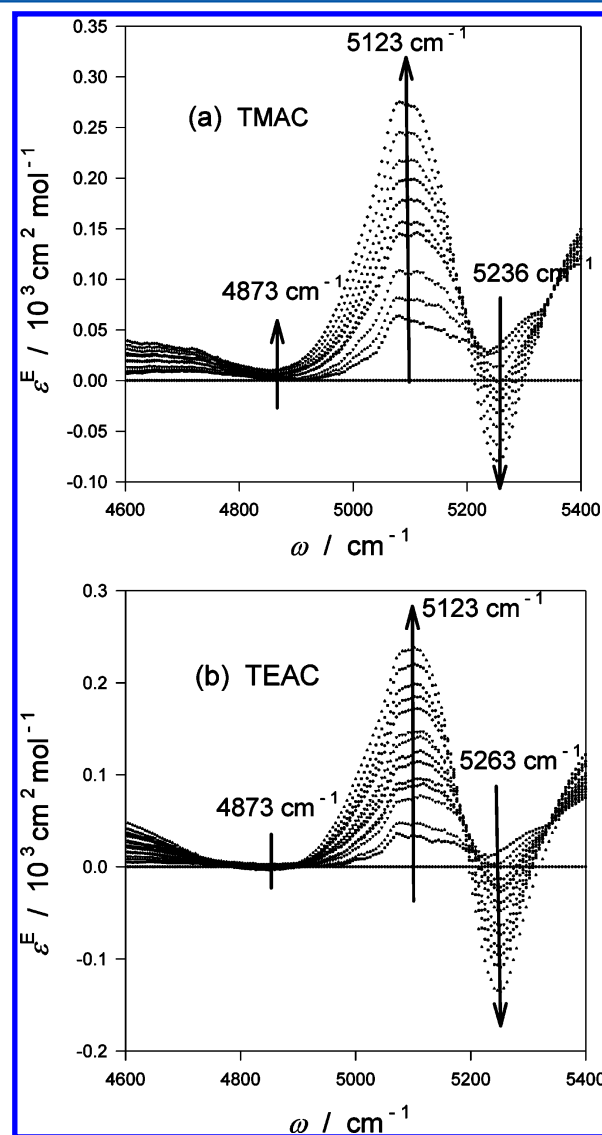


**Figure 4.** (a)  $x_S^0$  dependence of the  $x_{\text{IP}}$  loci of the peak top, point X, in  $H_{\text{IP}}^{\text{E}}$  patterns shown in Figure 3. The slope gives the hydrophobicity (hydration propensity) index. (b)  $x_S^0$  dependence of the  $H_{\text{IP}}^{\text{E}}$  loci of the peak top, point X, in  $H_{\text{IP}}^{\text{E}}$  patterns shown in Figure 3. The slope gives the hydrophilicity index.

X seem to be linear to  $x_S^0$ . Their slopes, therefore, can be regarded as the hydrophobicity and the hydrophilicity indices, respectively, for  $\text{TEA}^+\text{Cl}^-$ . Since we know equivalent indices for  $\text{Cl}^-$ ,<sup>24,38</sup> we are able to obtain them separately for the  $\text{TEA}^+$  ion. Figure 1 displays the point for  $\text{TEA}^+$  on the hydrophobicity/hydrophilicity map together with  $\text{TMA}^+$ ,  $\text{Na}^+$ ,<sup>26</sup> urea,<sup>39,40</sup>  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,<sup>24,38</sup>  $\text{NH}_4^+$ ,<sup>26,41</sup> and  $\text{DMSO}$ .<sup>36</sup>  $\text{TEA}^+$  is indeed an amphiphile with a small hydrophobic contribution. The result of the point for  $\text{TMA}^+$  relative to that for  $\text{NH}_4^+$  was discussed extensively earlier.<sup>23</sup> Briefly, the H atom of  $\text{CH}_3$  group attached to the highly electronegative N atom seems to become susceptible for hydrogen bonding to the surrounding  $\text{H}_2\text{O}$  molecules, and hence  $\text{TMA}^+$  apparently shows hydro-

philicity, as strong as urea. The present finding for  $\text{TEA}^+$  shown in Figure 1 is surprising! While  $\text{TEA}^+$  appears amphiphilic with a small hydrophobic contribution, its hydrophilicity index for  $\text{TEA}^+$  is about 2-fold stronger than that for  $\text{TMA}^+$  and urea! In terms of hydrophobicity,  $\text{TEA}^+$  is slightly hydrophobic as much as a half of that for  $\text{DMSO}$ , while that for  $\text{TMA}^+$  is zero right on the ordinate. To investigate these surprising results further, we studied the behavior of the  $\nu_2 + \nu_3$  spectra for aqueous TMAC and TEAC.

**Near-Infrared Spectroscopic Studies on Aqueous TMAC and TEAC.** As our previous studies on aqueous solutions of acetonitrile and acetone,<sup>27</sup> and Na-halides,<sup>28</sup> the  $\nu_2 + \nu_3$  combination band of  $\text{H}_2\text{O}$  was targeted.  $\nu_2$  is known to be due to the bending and  $\nu_3$  the asymmetric stretch vibration of  $\text{H}_2\text{O}$ . The absorbance data,  $A$ , are given in Table S2 and plotted in Figure S1 of the Supporting Information. The values of  $\epsilon^{\text{E}}$  were then calculated by eq 2 in order to make the nonideal contribution stand out. The literature density data<sup>13,14</sup> were used to calculate  $V_{\text{m}} = V/N$ . The results are shown in Figure 5.



**Figure 5.** (a) Spectra of the excess molar absorptivity,  $\epsilon^{\text{E}}$ , in aqueous TMAC, for given  $x_S$  ( $S = \text{TMAC}$ ) from 0 to 0.1. (b) Spectra of the excess molar absorptivity,  $\epsilon^{\text{E}}$ , in aqueous TEAC, for given  $x_S$  ( $S = \text{TEAC}$ ) from 0 to 0.1.

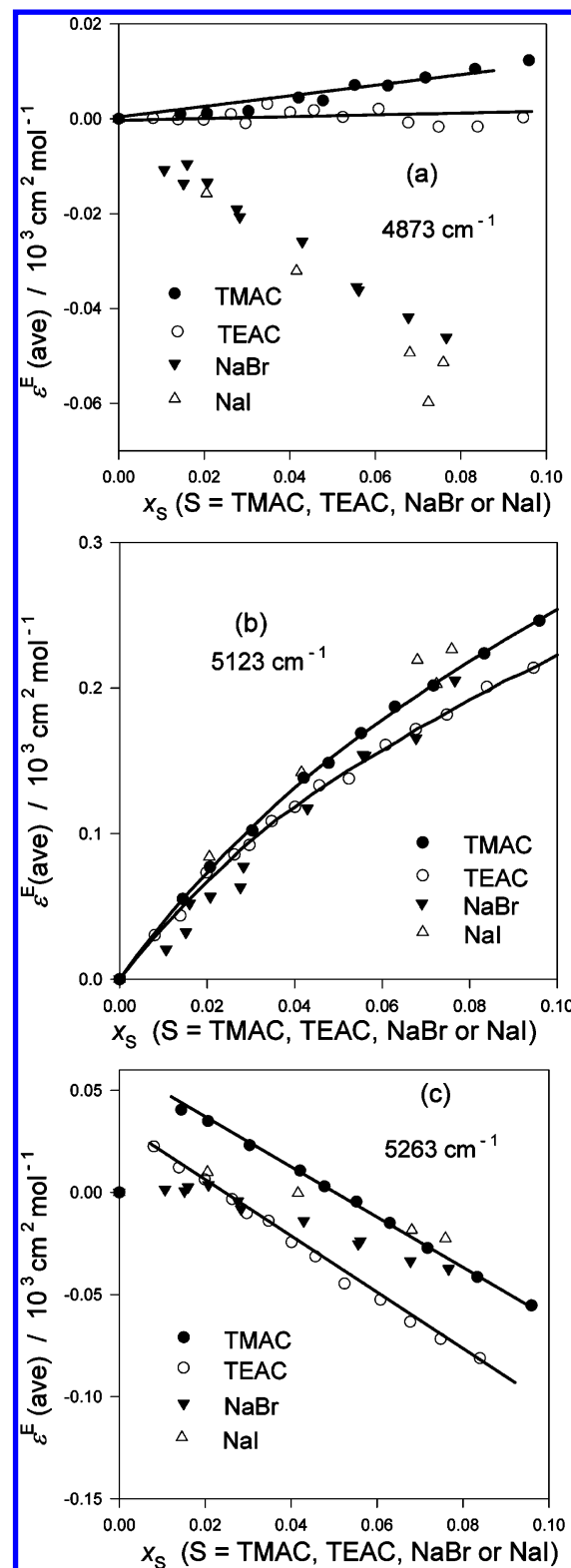


As for the case for aqueous Na halides,<sup>28</sup> the negative  $\epsilon^E$  band at 5263  $\text{cm}^{-1}$  and the positive one at 5123  $\text{cm}^{-1}$  are evident at the same wavenumbers for aqueous Na halides. As discussed above, these were attributed to free  $\text{H}_2\text{O}$  molecules under the influence of the charges of ions and to liquidlike  $\text{H}_2\text{O}$  chromophore, respectively. The previously recognized 4873  $\text{cm}^{-1}$  negative bands due to the solidlike portion of  $\text{H}_2\text{O}$  is almost nonexistent. This observation is not inconsistent with our findings by the 1P probing methodology that  $\text{TMA}^+$  and  $\text{TEA}^+$  are both hydrophilic (not hydrophobic), since hydrophobicity would show up in this solidlike chromophore according to the results for aqueous acetonitrile (a hydrophobe) versus acetone (a hydrophile)<sup>27</sup> mentioned in Introduction. The effect of counteranion  $\text{Cl}^-$  (a hydration center) on this chromophore would be rather small judging from the closeness to the origin in Figure 2. There could be a small difference in the value of  $\epsilon^E$ , however, in that it is more negative for TEAC than for TMAC. Taking into account a small negative hydrophobicity (hydration propensity) contribution from  $\text{Cl}^-$ ,<sup>28</sup> the effect of  $\text{TMA}^+$  on  $\epsilon^E$  is more positive than  $\text{TEA}^+$ . For Na halides,<sup>28</sup> their effects on  $\epsilon^E$  at this chromophore are in the order  $\text{Cl}^- > \text{Br}^- > \text{I}^-$ ; the larger the ion size and the hydrophilicity, the more negative the value of  $\epsilon^E$ . The same trend is evident for  $\text{TMA}^+ > \text{TEA}^+$  here.

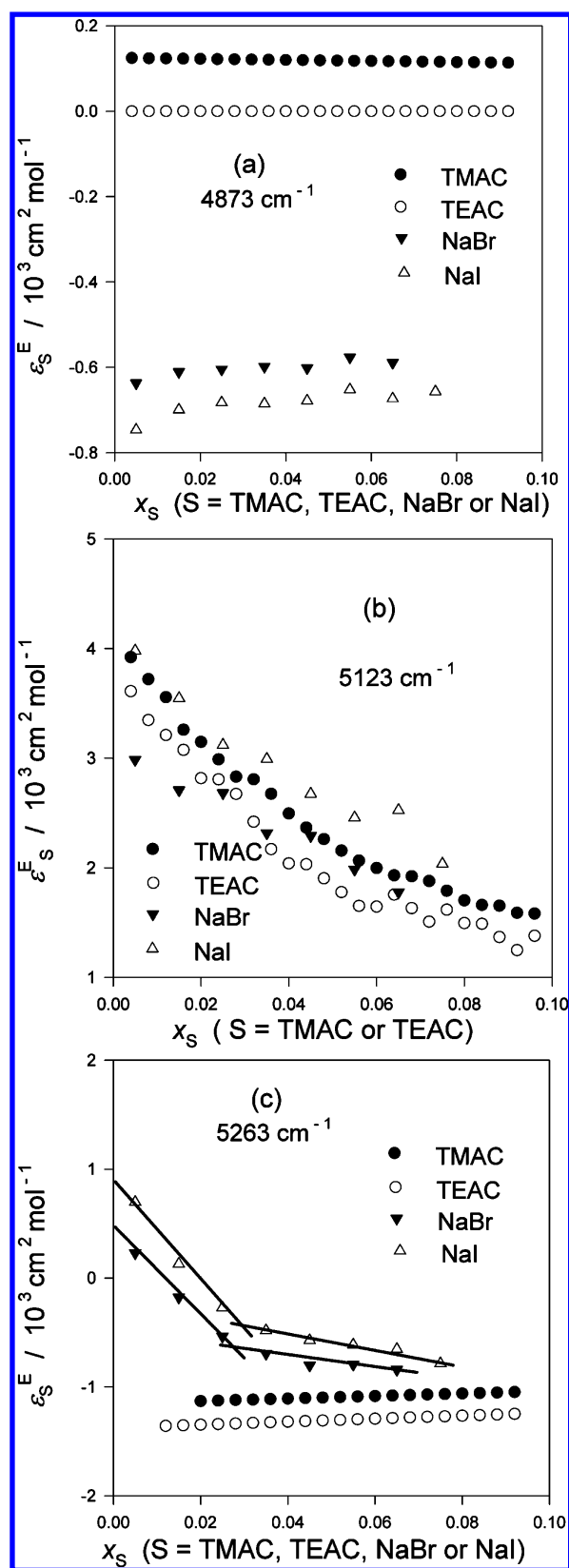
In order to investigate further the effect of solute on  $\epsilon^E$ , we next evaluate  $\epsilon^E_S$  by eq 3. We first take the average value of  $\epsilon^E$  of each band center within a narrow strip of  $\pm 30 \text{ cm}^{-1}$  for the purpose of smoothing random errors. It would be customary to integrate each band, but the spectrum of  $\epsilon^E$  is calculated by eq 2 which indicates that small absolute values of the resulting  $\epsilon^E$  will have a relatively large error due to subtraction of nearly the same values. Thus, we prefer to calculate the average  $\epsilon^E$  of the peak top only. This would avoid also an ambiguity about possible overlaps from adjacent bands. The resulting data of  $\epsilon^E(\text{ave})$  for each band are plotted in Figure 6. Smooth curves were drawn through the data points by aid of a flexible ruler. The values of  $\epsilon^E(\text{ave})$  were then read off the smooth curve drawn at the interval of  $\delta x_S = 0.004$ , and  $\epsilon^E_S$  were calculated by eq 3 with an approximation of the partial derivative of the far right of eq 3 with quotients  $\delta \epsilon^E(\text{ave})/\delta x_S$  for  $\delta x_S = 0.008$ . Appropriateness of such approximation was discussed extensively earlier.<sup>34</sup> The results are plotted in Figure 7 together with the same data for NaBr and NaI from the previous work<sup>28</sup> for comparison. The latter two Na halides are chosen since  $\text{Br}^-$  and  $\text{I}^-$  are close to  $\text{TMA}^+$  and  $\text{TEA}^+$  on the hydrophobicity/hydrophilicity map, Figure 1.

At 4873  $\text{cm}^{-1}$  due to solidlike  $\text{H}_2\text{O}$  molecules, the values of  $\epsilon^E_S$ , the effects of TMAC and TEAC on  $\epsilon^E$ , are small, Figure 7a, noting the scale of the ordinate and their little  $x_S$  dependence. This is consistent with the fact that  $\text{TMA}^+$  and  $\text{TEA}^+$  are both hydrophilic and that  $\text{Cl}^-$  is only marginally hydrated, according to the 1P-probing methodology. In comparison with the previous results of NaBr and NaI,<sup>28</sup> the main difference between the two sets in the figure could be due to the counterion  $\text{Na}^+$  being more hydrated (or hydrophobic) than  $\text{Cl}^-$ . The relative difference in the values of  $\epsilon^E_S$  between TMAC and TEAC is about the same as that for NaBr and NaI. Indeed, the relative southward shift from  $\text{Br}^-$  (G) to  $\text{I}^-$  (H) on the ordinate is about the same as that from  $\text{TMA}^+$  (E) to  $\text{TEA}^+$  (F) in the southward component.

For the 5123  $\text{cm}^{-1}$  chromophore of liquidlike  $\text{H}_2\text{O}$ , Figure 7b, the values of  $\epsilon^E_S$  for TMAC, TEAC, NaBr, and NaI are large (see the ordinate scale) and are all about the same with similar



**Figure 6.** (a) Average values of excess molar absorptivity,  $\epsilon^E(\text{ave})$ , at the peak top at  $4873 \pm 30 \text{ cm}^{-1}$  (the solidlike chromophore of  $\text{H}_2\text{O}$ ) for TMAC, TEAC, NaBr,<sup>28</sup> and NaI<sup>28</sup> against  $x_S$ . (b) Average values of excess molar absorptivity,  $\epsilon^E(\text{ave})$ , at the peak top at  $5123 \pm 30 \text{ cm}^{-1}$  (the liquidlike chromophore of  $\text{H}_2\text{O}$ ) for TMAC, TEAC, NaBr,<sup>28</sup> and NaI<sup>28</sup> against  $x_S$ . (c) Average values of excess molar absorptivity,  $\epsilon^E(\text{ave})$ , at the peak top at  $5263 \pm 30 \text{ cm}^{-1}$  (the gaslike chromophore of  $\text{H}_2\text{O}$ ) for TMAC, TEAC, NaBr,<sup>28</sup> and NaI<sup>28</sup> against  $x_S$ .



**Figure 7.** (a) Excess partial molar absorptivity of solute,  $\epsilon_S^E$ , at  $4873 \text{ cm}^{-1}$  (the solidlike chromophore) against  $x_S$ . (b) Excess partial molar absorptivity of solute,  $\epsilon_S^E$ , at  $5123 \text{ cm}^{-1}$  (the liquidlike chromophore) against  $x_S$ . (c) Excess partial molar absorptivity of solute,  $\epsilon_S^E$ , at  $5263 \text{ cm}^{-1}$  (the gaslike chromophore) against  $x_S$ .

$x_S$  dependences. This indicates that the effects of respective counterions  $\text{Na}^+$  and  $\text{Cl}^-$  on  $\epsilon^E$  do not show up at this wavenumber, and that ( $\text{TMA}^+$  and  $\text{TEA}^+$ ) and ( $\text{Br}^-$  and  $\text{I}^-$ ) pairs show about the same effects hinting also  $\text{TMA}^+$  and  $\text{TEA}^+$  to act as “hydrophiles” as  $\text{Br}^-$  and  $\text{I}^-$ . The value of  $\epsilon_S^E$  for  $\text{TMA}^+$  is larger than that for  $\text{TEA}^+$  while that for  $\text{Br}^-$  is smaller than for  $\text{I}^-$ ; in terms of  $\epsilon_S^E$   $\text{TMAC} > \text{TEAC}$  and  $\text{NaBr} < \text{NaI}$ . Aside from the obvious difference in the sign of charge, the ionic size and the locus of the map indicate  $\text{I}^- > \text{Br}^-$  and  $\text{TEA}^+ > \text{TMA}^+$ . Clearly, further theoretical or other modern spectroscopic studies are required to sort out this discrepancy.

Figure 7c shows the  $\epsilon_S^E$  for  $5263 \text{ cm}^{-1}$  band, which was ascribed to be free gaslike species of  $\text{H}_2\text{O}$  without hydrogen bonds under the influence of the electric charges of ions. For NaBr and NaI, breaks in slope are apparent at about  $x_S = 0.03$  in Figure 7c.<sup>28</sup> Namely, the effect of salt on  $\epsilon^E$  slows down rather suddenly at the break points. They were attributed to some form of aggregation, perhaps  $\text{H}_2\text{O}$ -mediated ion pairings.<sup>37,42,43</sup> In comparison, TMAC and TEAC show very little  $x_S$  dependences similar to the Na halides case after the ion pairing. This may hint that, for both TMAC and TEAC, the solutes might be already aggregated as aqueous DMSO,<sup>37</sup> as discussed above regarding Figure 3b. Indeed, recent X-ray scattering experiments on TMA and TEA bromides at about 1.5 M ( $x_S \sim 0.03$ ) suggested self-aggregation.<sup>12</sup> We note, however, that the trend of the values of  $\epsilon_S^E$  from NaBr to NaI is reverse of that from TMAC to TEAC, which is not in the order of ion size, aside from the charge sign difference. There is a theoretical calculation on the effect of ionic field on the symmetric stretch  $\nu_1$  for  $\text{H}_2\text{O}$ .<sup>44</sup> A similar theoretical study for the  $\nu_2 + \nu_3$  band is awaited.

Thus, we presented here two sets of experimental results that could be interpreted as showing hydrophilicity, rather than hydrophobicity, for  $\text{TMA}^+$  and  $\text{TEA}^+$  cations and that the latter is more “hydrophilic” than the former, more consistent with the minority conclusion.<sup>13,14</sup> There is also an indication that both TMAC and TEAC form small aggregates in the  $\text{H}_2\text{O}$ -rich region of their aqueous solutions.

An important question remains why the conclusions about the effect of  $\text{R}_4\text{N}^+$  are contradictory among a large number of investigations. While a number of possibilities could be responsible (for example, time scale of the experimental technique used), the reality is a holistic object and each conclusion shed a light on a limited facet of the object. When we come a step closer to the truth, then some conclusions could be reconciled. Another source of controversy could be our automatic impression that alkyl groups are without fail the source of hydrophobicity toward  $\text{H}_2\text{O}$ . The present work together with earlier one<sup>23</sup> casts some caution in choosing N-alkyl groups, alkyl moieties attached to N, for a typical hydrophobe which in fact showed “hydrophilicity” within our 1P-probing methodology and that using the excess partial molar absorptivity of solute on the  $\nu_2 + \nu_3$  band of  $\text{H}_2\text{O}$ .

In this work, we limited ourselves to  $\text{Cl}^-$  ion for the counterion. Krienke et al. used the explicit water molecular dynamics simulation to study  $\text{TMA}^+$  and  $\text{TEA}^+$  with both  $\text{Cl}^-$  and  $\text{Br}^-$  as counteranions, and showed that the first peak of  $\text{TMA}^+ - \text{Br}^-$  distribution function is much larger than that of the  $\text{Cl}^-$  counterpart.<sup>45</sup> We noted in a previous 1P-probing and NIR study that  $\text{Cl}^-$  is a hydration center without perturbing the bulk  $\text{H}_2\text{O}$  away from the hydration shells, while  $\text{Br}^-$  is a hydrophile with a similar hydrophilicity as  $\text{TMA}^+$ . See the hydrophobicity/hydrophilicity map (Figure 1). Furthermore,

we showed that the qualitative difference between  $\text{Cl}^-$  and  $\text{Br}^-$  is evident only in the  $5123\text{ cm}^{-1}$  band due to liquidlike  $\text{H}_2\text{O}$ .<sup>28</sup> This may be related to the findings by Krienke et al., but the detailed mechanistic connection is yet to be elucidated. Taking into account the well-known fact that the ion effects of anions are stronger than those by cations in the Hofmeister rankings,<sup>46</sup> anion effects ought to be paid more attention in studying a salt's effect on aqueous solutions. Here, we showed the surprising hydrophilic propensities of  $\text{TMA}^+$  and  $\text{TEA}^+$  cations.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Appendices A and B are given, together with Figure S1, NIR spectra. In addition Table S1 containing the values of  $H_{\text{IP}}^{\text{E}}$  and Table S2 with absorbance data are given as separate Excel files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Huot, J.-Y.; Jolicoeur, C. *The Chemical Physics of Solvation. Part A. Theory of Solvation*; Dogonadze, R. R., Kalman, E., Kornyshev, A. A., Ulstrup, J., Eds.; Elsevier: Amsterdam, 1985; Chapter 11, pp 417–471.
- (2) Lindenbaum, S.; Boyd, G. E. *J. Phys. Chem.* **1984**, *68*, 911–917.
- (3) Sharp, K. A.; Madan, B.; Manas, E.; Vanderkooi, J. M. *J. Chem. Phys.* **2001**, *114*, 1791–1796.
- (4) Gallagher, K. R.; Sharp, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 9853–9860.
- (5) Stranglet, J.; Gampe, T. *J. Phys. Chem. B* **1999**, *103*, 3778–3783.
- (6) Finney, J. L.; Soper, A. K. *Chem. Soc. Rev.* **1994**, *23*, 1–10.
- (7) Turner, J. Z.; Soper, A. K. *J. Chem. Phys.* **1994**, *101*, 6116–6125.
- (8) Turner, J. Z.; Soper, A. K.; Finney, J. L. *J. Chem. Phys.* **1995**, *102*, 5438–5443.
- (9) Buchner, R.; Holz, C.; Stauber, J.; Barthel, J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 2169–2179.
- (10) Salamanca, Y. P.; Blanco, L. H.; Buchner, R.; Vargas, E. F. *J. Chem. Eng. Data* **2012**, *57*, 2203–2210.
- (11) Kustov, A. V.; Korelev, V. P. *J. Phys. Chem. B* **2008**, *112*, 2040–2044.
- (12) Huang, A. V.; Sohlessinger, D.; Nordlund, D.; Huang, C.; Pettersson, L. G. M.; Nilsson, A. *J. Chem. Phys.* **2012**, *136* (074507), 1–7.
- (13) Jakli, G.; Jerie, K.; Barnowski, A.; Glinski, J. *Acta Phys. Pol., A* **1998**, *93*, 649–658.
- (14) Jerie, K.; Baranowski, A.; Jakli, G.; Glinski, J. *J. Radioanal. Nucl. Chem.* **1999**, *240*, 223–229.
- (15) Underwood, R.; Tomlinson-Phillips, J.; Ben-Amotz, D. *J. Phys. Chem. B* **2010**, *114*, 8646–8651.
- (16) Zhong, Y.; Patel, S. J. *Phys. Chem. B* **2010**, *114*, 11076–11092.
- (17) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter I, Section 8.
- (18) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter VI, Section 1, pp 151–155.
- (19) Koga, Y. *Netsu Sokutei (J. Jpn. Soc. Calor. Therm. Anal.)* **2003**, *30*, 54–65; ISSN 0386-2615. Available in PDF form on request from the author, [koga@chem.ubc.ca](mailto:koga@chem.ubc.ca).
- (20) Koga, Y. *J. Phys. Chem.* **1996**, *100*, 5172–5182.
- (21) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapters VII and VIII, pp 175–239.
- (22) Koga, Y. *Netsu Sokutei* **2007**, *34*, 3–13. Available in PDF form on request from the author, [koga@chem.ubc.ca](mailto:koga@chem.ubc.ca).
- (23) Koga, Y.; Westh, P.; Nishikawa, K.; Subramanian, S. *J. Phys. Chem. B* **2011**, *115*, 2995–3002.
- (24) Westh, P.; Kato, H.; Nishikawa, K.; Koga, Y. *J. Phys. Chem. A* **2006**, *110*, 2072–2078.
- (25) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter VIII, Section 5, pp 225–229.
- (26) Koga, Y.; Katayanagi, H.; Davies, J. V.; Kato, H.; Nishikawa, K. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1347–1354.
- (27) Koga, Y.; Sebe, F.; Minami, T.; Otake, K.; Saitow, K.; Nishikawa, K. *J. Phys. Chem. B* **2009**, *113*, 11928–11935.
- (28) Sebe, F.; Nishikawa, K.; Koga, Y. *Phys. Chem. Chem. Phys.* **2012**, *14*, 4433–4439.
- (29) Nikolova, P.; Duff, S. J. B.; Westh, P.; Haynes, C. A.; Kasahara, Y.; Nishikawa, K.; Koga, Y. *Can. J. Chem.* **2000**, *78*, 1553–1560.
- (30) Chen, D. H. C.; Chu, P. M.; E., C. H.; Koga, Y. *Fluid Phase Equilib.* **2000**, *175*, 35–43.
- (31) Fornes, V.; Chaussidon, J. *J. Chem. Phys.* **1978**, *68*, 4667–4671.
- (32) Koga, Y. *J. Chem. Phys.* **2012**, *137* (124503), 1–5.
- (33) Saitow, K.; Kobayashi, K.; Nishikawa, K. *J. Solution Chem.* **2004**, *33*, 689–698.
- (34) 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*, 1007–1028.
- (35) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter VII, Section 1, pp 175–179.
- (36) Morita, T.; Westh, P.; Nishikawa, K.; Koga, Y. *J. Phys. Chem. B* **2012**, *116*, 7328–7333.
- (37) Koga, Y.; Kasahara, Y.; Yoshino, K.; Nishikawa, K. *J. Solution Chem.* **2001**, *30*, 885–893.
- (38) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter VIII, Section 2 and 3, pp 207–217.
- (39) Koga, Y.; Miyazaki, Y.; Nagano, Y.; Inaba, A. *J. Phys. Chem. B* **2008**, *112*, 11341–11346.
- (40) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007. Chapter VII, Section 3, pp 187–192.
- (41) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter VIII, Section 5, pp 225–229.
- (42) Buchner, R.; Hefter, G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8984–8999.
- (43) Vazder, M.; Uhlig, F.; Jungwirth, P. *J. Phys. Chem. Lett.* **2012**, *3*, 2021–2024.
- (44) Smith, J. D.; Saykally, R. T.; Geissler, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 13847–13856.
- (45) Krienke, H.; Vlady, V.; Ahn-Ercan, G.; Bako, I. *J. Phys. Chem. B* **2009**, *113*, 4360–4371.
- (46) Koga, Y. *Solution Thermodynamics and Its Application to Aqueous Solutions: A Differential Approach*; Elsevier: Amsterdam, 2007; Chapter VIII, Section 1, pp 205–206.