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Spectrum of excess partial molar absorptivity. Part II: a near infrared spectroscopic study of aqueous Na-halides†

Fumie Sebe,‡[a] Keiko Nishikawa[a] and Yoshikata Koga*[b]

Our earlier thermodynamic studies suggested that F^- and Cl^- form hydration shells with the hydration number 14 ± 2 and 2.3 ± 0.6, respectively, and leave the bulk H_2O away from hydration shells unperturbed. Br^- and I^-, on the other hand, form hydrogen bonds directly with the momentarily existing hydrogen bond network of H_2O, and retard the degree of entropy–volume cross fluctuation inherent in liquid H_2O. The effect of the latter is stronger for I^- than Br^-. Here we seek additional information about this qualitative difference between Cl^- and (Br^- and I^-) pair by near infrared (NIR) spectroscopy. We analyze the $\nu_2 + \nu_3$ band of H_2O in the range 4600–5500 cm^{-1} of aqueous solutions of NaCl, NaBr and NaI, by a new approach. From observed absorbance, we calculate excess molar absorptivity, ε^E, excess over the additive contributions of solute and solvent. ε^E thus contains information about the effect of inter-molecular interactions in the $\nu_2 + \nu_3$ spectrum. The spectrum of ε^E shows three bands; two negative ones at 5263 and 4873 cm^{-1}, and the positive band at 5123 cm^{-1}. We then define and calculate the excess *partial* molar absorptivity of each salt, ε^E_{salt}. From the behaviour of ε^E_{salt} we suggest that the negative band at 5263 cm^{-1} represents free H_2O without much hydrogen bonding under the influence of local electric field of ions. Furthermore, from a sudden change in the x_{salt} (mole fraction of salt) dependence of ε^E_{salt}, we suggest that there is an ion-pairing in $x_{salt} > 0.032$, 0.036, and 0.04 for NaCl, NaBr and NaI respectively. The positive band of ε^E at 5123 cm^{-1} is attributed to a modestly organized hydrogen bond network of H_2O (or liquid-likeness), and the x_{salt} dependence of ε^E_{salt} indicated a qualitative difference in the effect of Cl^- from those of Br^- and I^-. Namely, the values of ε^E_{salt} stay constant for Cl^- but those for Br^- and I^- decrease smoothly on increasing the salt mole fraction. The mole fraction dependence of ε^E_{salt} at the 4873 cm^{-1} band, due to ice-likeness in H_2O, shows a subtle difference between Cl^- and (Br^-, I^-) pair.

Introduction

No emphasis is required for the importance of detailed studies on the hydrogen bonding characteristics in aqueous solutions of electrolytes. Indeed, there are a large number of studies on the subject using modern advanced spectroscopic techniques such as ultra fast optical Kerr effect measurement,[1] X-ray Raman and small angle scattering,[2] oxygen K-edge absorption spectroscopy,[3] steady state and ultra fast vibrational spectro-scopy aided by simulation,[4,5] and femto-second pump–probe mid-infrared spectroscopy[6] to name but a few. These studies now have established the presence of hydration shells around ions. Another consensus from these modern studies is that all the ions studied so far do not alter the hydrogen bond characteristics of bulk H_2O away from the hydration shell, very little if any. These authors thus suggest that such a classical qualitative distinction of various ions in terms of "structure maker/breaker" is no longer meaningful. In turn, the "kosmo-/chao-trope" distinction for ions in the Hofmeister series[7] must be sought not on the effects of ions on H_2O, but rather on specific direct interactions of the ion with the biopolymer in question.[8] Indeed, recent surge of papers on the Hofmeister effects is remarkable.[9–16]

However, the Hofmeister rankings are surprisingly ubiqui-tous, particularly for anions, among different physical/chemical processes involving a variety of biopolymers, colloids *etc.* Therefore, there must be some effects of ions on bulk H_2O away from the first hydration shell, which affects the ranking. Indeed, a recent infrared photodissociation study on $SO_4^{2-}(H_2O)_n$ clusters indicated that a SO_4^{2-} ion, a typical kosmotrope in the Hofmeister series, does affect bulk H_2O beyond the first hydration shell.[17]

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† Electronic supplementary information (ESI) available: Table S1: absorbance, A, and excess molar absorptivity, ε^E. Fig. S1(d)–(f): coloured plots of A against wave number ω. See DOI: 10.1039/c2cp23255c
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Phys. Chem. Chem. Phys., 2012, **14**, 4433–4439 | 4433

We have characterized a number of ions in terms of their specific thermodynamic effects on the molecular organization of H_2O.[18a,b,11–30] In particular, we concluded that Na^+, F^- and Cl^- ions are hydrated by 5.2, 14 ± 2, and 2.3 ± 0.6 molecules of H_2O, respectively, and more importantly leave the bulk H_2O away from hydration shells unperturbed.[18b,24] This is consistent with the conclusions by the modern spectroscopic studies mentioned above.[1–6] Our findings on Br^-, I^-, and other chaotropic ions, on the other hand, are at odds with the conclusions by the above spectroscopic studies. Namely, we found that they form hydrogen bonds directly with the existing hydrogen bond network of H_2O and act as impurities within the network. By doing so, they break H donor/acceptor symmetry enjoyed in pure H_2O and hence retard the degree of fluctuation inherent in pure liquid H_2O. Such an effect of I^- is stronger than that of Br^-.[18c,d,24] For the halide ions, they are known to form hydrogen bonds with H_2O and their strength is ranked as $F^- > Cl^- > Br^- > I^-$.[31,32] Our findings above indicate that the first two halogen ions are strong enough for stripping a number of H_2O molecules from the hydrogen bond network of H_2O and form hydration shells with $n_H = 14 ± 2$ and 2.3 ± 0.6 respectively. For Br^- and I^-, their hydrogen bond forming tendencies are weaker and they only participate in direct hydrogen bonding with the existing hydrogen bond network of H_2O.[18d,24] To the best of our knowledge, such a qualitative distinction between (F^-, Cl^-) and (Br^-, I^-) pairs is not clearly forwarded by spectroscopic studies, certainly not by modern studies[1–6] as mentioned above.

Here we attempt at gaining a deeper insight by a near infrared (NIR) spectroscopic study of aqueous solutions of Na-salts of Cl^-, Br^-, and I^-. We seek additional information as to which vibrational chromophore is responsible for the qualitative difference between Cl^- and (Br^-, I^-). We follow the differential approach we used in solution thermodynamics and succeeded in gaining a deeper insight into the molecular processes in aqueous solutions.[18,19,29,30] As shown in the previous NIR study of the $\nu_2 + \nu_3$ band of H_2O in aqueous acetonitrile and acetone,[33] we use the excess partial molar absorptivity of a solute. (ν_2 is known to be the bending and ν_3 the asymmetric vibration modes.) We demonstrated the power of this approach in gaining additional insight into the difference in the mixing scheme between aqueous acetonitrile (a hydrophobe)[18c,23] and acetone (a hydrophile) found earlier.[18b,c,34,35] Namely we found from our earlier NIR study[33] that hydrophobic acetonitrile reduces the transition moment in the lower wave number portion in the $\nu_2 + \nu_3$ band of H_2O, corresponding to ice-like portion, or more hydrogen bonding, while hydrophilic acetone increases the intensity of the spectrum of the higher wave number region (liquid-like with lesser hydrogen bonding).[33] Here we apply the same approach to NIR spectra of aqueous NaCl, NaBr and NaI, and seek any additional information relative to the qualitative difference in the Cl^- and (Br^-, I^-) pair that we found by a differential approach in solution thermodynamics.[18b,24] We first reiterate the concept of the excess partial molar absorptivity of a solute.

Excess partial molar absorptivity

Details are given earlier.[33] Briefly, the absorbance, A, as a function of the wave-number, ω, for the binary mixture consisting of n_B of B and n_W of W is written down following the solution thermodynamics tradition as,[36]

$$A/l = \varepsilon(N/V) = \varepsilon_B^0(n_B/V) + \varepsilon_W^0(n_W/V) + \varepsilon^E(N/V), \quad (1)$$

where l is the optical path length, and $N = n_B + n_W$ is the total molar amount in the volume V through which the light passes. With the molar volume $V_m = V/N$, eqn (1) is rewritten as,

$$(A/l)V_m = \varepsilon = x_B\varepsilon_B^0 + x_W\varepsilon_W^0 + \varepsilon^E, \quad (2)$$

where $x_B = n_B/N$ and $x_W = n_W/N$, the mole fraction of B and W respectively. In the present case, B represents NaCl, NaBr or NaI, and ε_B^0 is zero in the 4600 to 5500 cm^{-1} range. ε_W^0 is determined using pure H_2O. ε^E thus calculated contains all the information about the non-ideality of the mixture through its ω and x_B dependences, just as an excess thermodynamic function, the excess enthalpy of the system, H^E, for example. (Of course, H^E is devoid of the ω-dependence, hence ε^E provides additional information via ω-dependence.)

The conventional approach in spectroscopic data analysis is to regard the total molar absorptivity as,

$$(A/l)V_m = \varepsilon = \Sigma x_i\varepsilon_i^0, \quad (3)$$

instead of eqn (2). ε_i^0 and x_i are the molar absorptivity and the mole fraction of the i-th species respectively. In this treatment, i could stand for such putative species as a hydration species of $B(H_2O)_n$ type,[37] or H_2O molecules distinguished by the number of hydrogen bonds to the central O atom,[38–40] as well as actual chemical species B and W. The presence of such putative species is assumed at the outset for this type of analysis by using eqn (3). In this type of treatment, the non-ideality of the system is attributed to the presence of such putative species.

In the present analysis based on eqn (2), there are no a priori assumptions, and the non-ideality is lumped together in ε^E, which is the excess quantity over that of an ideal B–W system without any interactions. We point out that this quantity is obtained purely experimentally without any assumptions. Thus ε^E contains all the information about the holistic result coming from molecular interactions in the system. In order to make the x_B-dependence on ε^E more clear, we proposed to define and calculated the excess partial molar absorptivity of B, ε_B^E, as,

$$\varepsilon_B^E = N(\partial \varepsilon^E/\partial n_B)_{n_W} = (1 - x_B)(\partial \varepsilon^E/\partial x_B)_N. \quad (4)$$

The second equality and the factor N in the right of the first are for convenience of using the mole fraction scale. With this definition, ε_B^E indicates how ε^E of the $\nu_2 + \nu_3$ band is altered by an infinitesimal increase in n_B keeping n_W constant. Thus, it signifies how ε^E, or the excess part of the transition moment of the $\nu_2 + \nu_3$ band, is affected at the given value of ω on an infinitesimal increase of n_B keeping n_W constant. This in turn provides information about how the vibrational wave functions of the ground and/or the excited sates are modified at this wave number ω. The recognition that (A/l) is not necessarily linear to the concentration (N/V) and the suggestion that the differential molar absorptivity should be used were first pointed out by Ikehata.[41] He subsequently applied this concept to the $\nu_1 + \nu_3$ band of H_2O at about 7000 cm^{-1} of aqueous alcohols and concluded that alcohols enhance the hydrogen bond network.[42,43]

Experimental

An NIR spectrometer was home-built. The detail is described elsewhere.[38] It is of a single beam construction and we employed cells with an optical path length, l, of 0.25 mm. Absorbance, $A = \log[(t - t_d)/(t_0 - t_d)]$ was measured in the range from 4600 to 5500 cm^{-1} at about 3 cm^{-1} intervals. t is the transmittance, where subscript 0 stands for the incident, and d for the dark background, and none for the sample mixture. The spectrometer being of a single beam construction,[38] the measurements for t, t_d, and t_0 were not made concurrently. Hence there is an inevitable danger of introducing a systematic error resulting in upward or downward shifts of the base line. Several spectra that seemed to suffer such effects were removed prior to data analysis.

NaCl (Wako, 99%), NaBr (Wako, 99.5%), NaI (Wako, 99.5%) and H$_2$O (Wako) were used as supplied. The salts were dissolved gravimetrically using samples from freshly opened bottles, and diluted again gravimetrically prior to use. The densities of each sample solutions were interpolated using the literature data.[44]

Results and discussion

The absorbance data, A, are deposited as Table S1 (ESI†) and plotted in Fig. 1(a)–(c). (See also coloured graphs, Fig. S1(d)–(f) in ESI.†) In aqueous solutions of acetonitrile and acetone, the values of A decreased in the entire ω range from 4600 to 5500 cm^{-1} on addition of solutes.[33] In contrast, when Na-halides are added, A at about 5150 cm^{-1} increases but both the sides of the band decrease in intensity, more sharply on the blue than the red side. Namely, as the mole fraction of salt, x_{salt}, increases (indicated by three arrows in the figures), the values of absorbance, A, at the regions centered about 4873 cm^{-1} and 5263 cm^{-1} decrease while that at 5123 cm^{-1} increases. The boundaries between the decreasing regions and the central increasing one are at about 5000 cm^{-1} and 5200 cm^{-1}. These increases and decreases are no doubt due to intermolecular interactions and show the effects of each salt on the $\nu_2 + \nu_3$ band of H$_2$O. To see the latter effects more clearly, we calculate ε^E by eqn (2). In this manner, we remove the contribution from the hypothetical ideal solution and isolate the non-ideality of the mixture. The resulting ε^E spectra are given in Table S1 (ESI†) and plotted in Fig. 2. It is evident from the figure that there are three bands; two negative bands at about 5263 (200) and 4873 (100) cm^{-1}, and a positive one at about 5123(100) cm^{-1} for all three Na-halides. The numbers in ( ) are approximate half widths of each band. It is striking that the effects of Na-halides on the non-ideality of the system evident on the $\nu_2 + \nu_3$ band of H$_2$O are concentrated in these three ω-ranges. Namely, the effect of Na-halides is such that the excess portion of the transition moment, ε^E, of the $\nu_2 + \nu_3$ band is altered in a negative manner at 5263 and 4873 cm^{-1} and positively at 5123 cm^{-1} ω-ranges only. This is an important finding.

Next, we recall that in aqueous acetonitrile and acetone,[33] there was not a negative band at 5263 cm^{-1}. Rather, there were the positive band at 5230 (150) cm^{-1} that was attributed to the liquid-like part of H$_2$O, and the negative one at 5020 (250),

the ice-like portion of H$_2$O. This interpretation came directly from the experimental observation made by Fornes and Chaussidon that the $\nu_2 + \nu_3$ band for ice peaked at 5000 cm^{-1} and that for liquid at 5200 cm^{-1}.[39] The spectra of ε^E for acetonitrile are reproduced in Fig. 2(d) for comparison. Thus, in the present aqueous Na-halides, it appears that the positive and the negative bands of acetonitrile case red-shifted by about 100 cm^{-1} and a new negative band appeared at 5263 cm^{-1}. No doubt this clear distinction between aqueous acetonitrile vs. aqueous Na-halides provides important information about the effects of charges of ions on H$_2$O. While the distinction between aqueous electrolytes and non-electrolytes is qualitatively clear in the spectra of ε^E, Fig. 2(d) vs. Fig. 2(a)–(c), the distinction in the effect on ε^E between Cl$^-$ vs. (Br$^-$, I$^-$) apparent by our previous thermodynamic[18b,24] studies is not immediately obvious though there are some hints in Fig. 2. The next derivative, the excess partial molar absorptivity of salt, ε^E_{salt}, defined by eqn (4), could make such a distinction stand out.

In order to obtain ε^E_{salt}, we first take average value of ε^E of each band within ± 30 cm^{-1} of the peak top for the purpose of smoothing random errors. This, of course, is based on the observation that ε^E show three distinct bands in Fig. 2. In calculating ε^E, the relative error in the tail regions (the value of A being near zero) is larger than that near the peak. Hence, we take average of A in the strip of ± 30 cm^{-1} of the peak, rather than integrating peak areas. This would avoid an ambiguity due to possible overlaps from the adjacent peaks. The resulting data of ε^E(ave) at each ω-value of three bands are plotted in Fig. 3. Hereinafter, we limit ourselves to the mole fraction range, $x_{salt} < 0.047$ for Cl$^-$, $x_{salt} < 0.070$ for Br$^-$, and $x_{salt} < 0.072$ for I$^-$, since our previous thermodynamic study for Na-halides that we wish to make reference to was limited within these mole fraction ranges.[18b,24] (As mentioned above, we learned that the mixing scheme, the details of molecular arrangement in aqueous solution, is crucially dependent on the solute concentration.[18c,29,30]) From the smooth curves drawn as shown in Fig. 3, we graphically differentiate without resorting to any fitting function and evaluate ε^E_{salt}.[18c,27] The values of ε^E_{salt} are plotted for each band in Fig. 4.

At the 5263 cm^{-1} ω-region, Fig. 4(a) indicates that the effects of halides on ε^E with the counter cation fixed at Na$^+$ are only quantitatively different. While more data closely spaced in x_{salt} are desirable, the values of ε^E_{salt} start at $x_{salt} = 0$ with about 0, 450, and 900 cm^2 mol^{-1} for Cl$^-$, Br$^-$ and I$^-$, respectively, and all these ε^E_{salt} values decrease with almost the same slope on increasing x_{salt} up to about $x_{salt} = 0.032$, 0.036 and 0.040 for Cl$^-$, Br$^-$ and I$^-$ respectively. This seems to suggest that the effect of halide ions is to reduce the value of ε^E_{salt} in the order of charge density, Cl$^-$ > Br$^-$ > I$^-$. Also from the fact that we did not observe a negative band in ε^E at this ω-region for acetonitrile and acetone,[33] we suggest that this band is due to the presence of an electric field by ions, without showing a qualitative difference between Cl$^-$ and (Br$^-$, I$^-$). Furthermore, the $\nu_2 + \nu_3$ band for ice is known to be at 5000(400) cm^{-1} and that of liquid at 5200(250) cm^{-1}, and both blue shift on temperature increase.[39] Thus, this 5263 cm^{-1} region, blue-shifted by about 60 cm^{-1}, could represent free H$_2$O molecules with lesser degree of hydrogen bonding under the influence of a local electric field of ions. The dipole of free H$_2$O may be aligned such that the
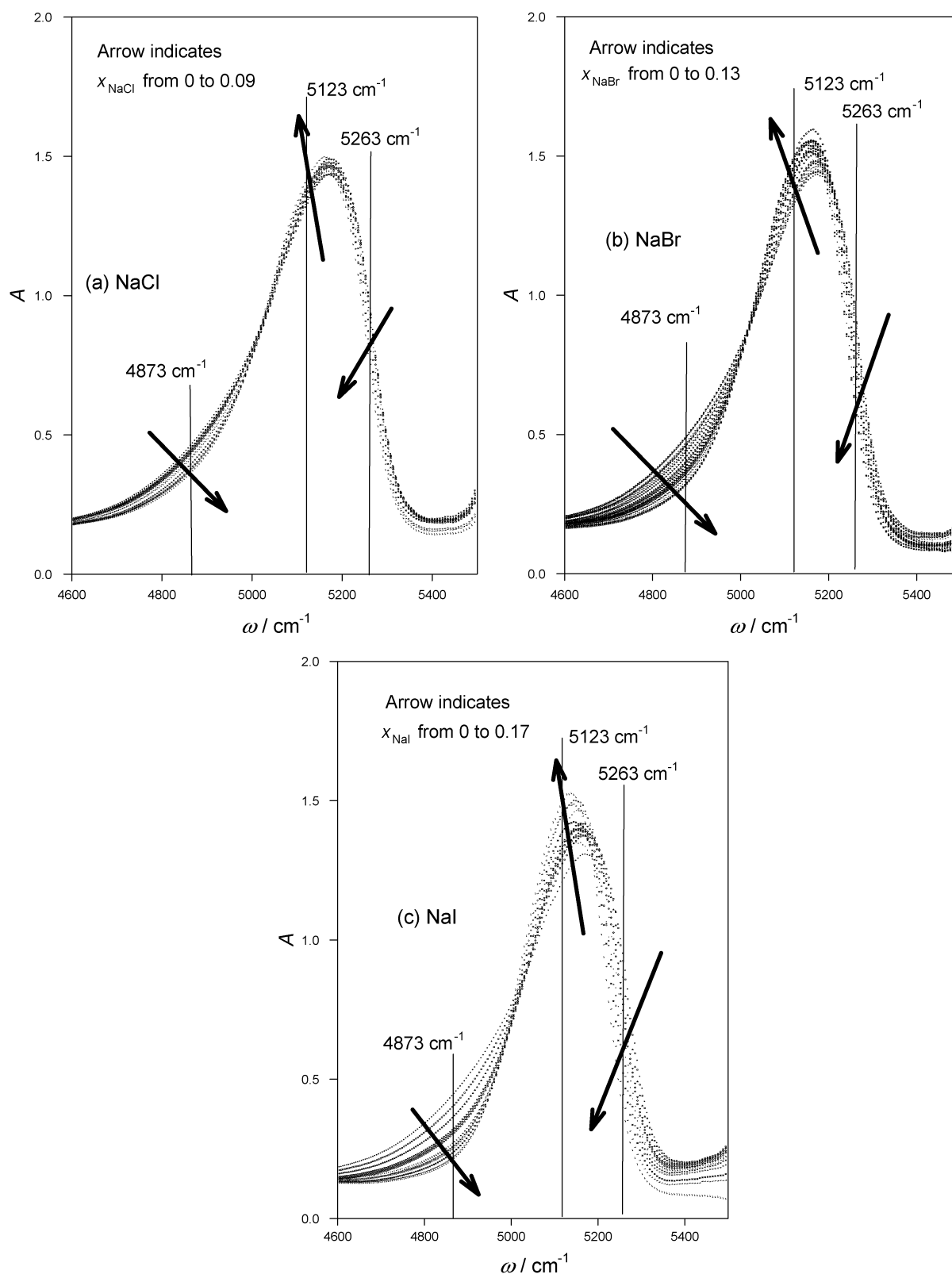
Fig. 1 (a) Absorbance, A, for NaCl. (b) Absorbance, A, for NaBr. (c) Absorbance, A, for NaI.

transition moment apparently decreases. Alternatively, the polarizability of these anions is in the reverse order, $Cl^- <$ $Br^- < I^-$, and this could well be related to the quantitative difference observed in Fig. 4(a). There is a theoretical study on

the effect of ionic field on the symmetric OH stretching band ν_1,[5] and a similar theoretical study for the $\nu_2 + \nu_3$ band of free H_2O is awaited. Another important point to note in Fig. 4(a) is that the slopes of initial decreases of ε_{salt}^E show breaks along the dotted line
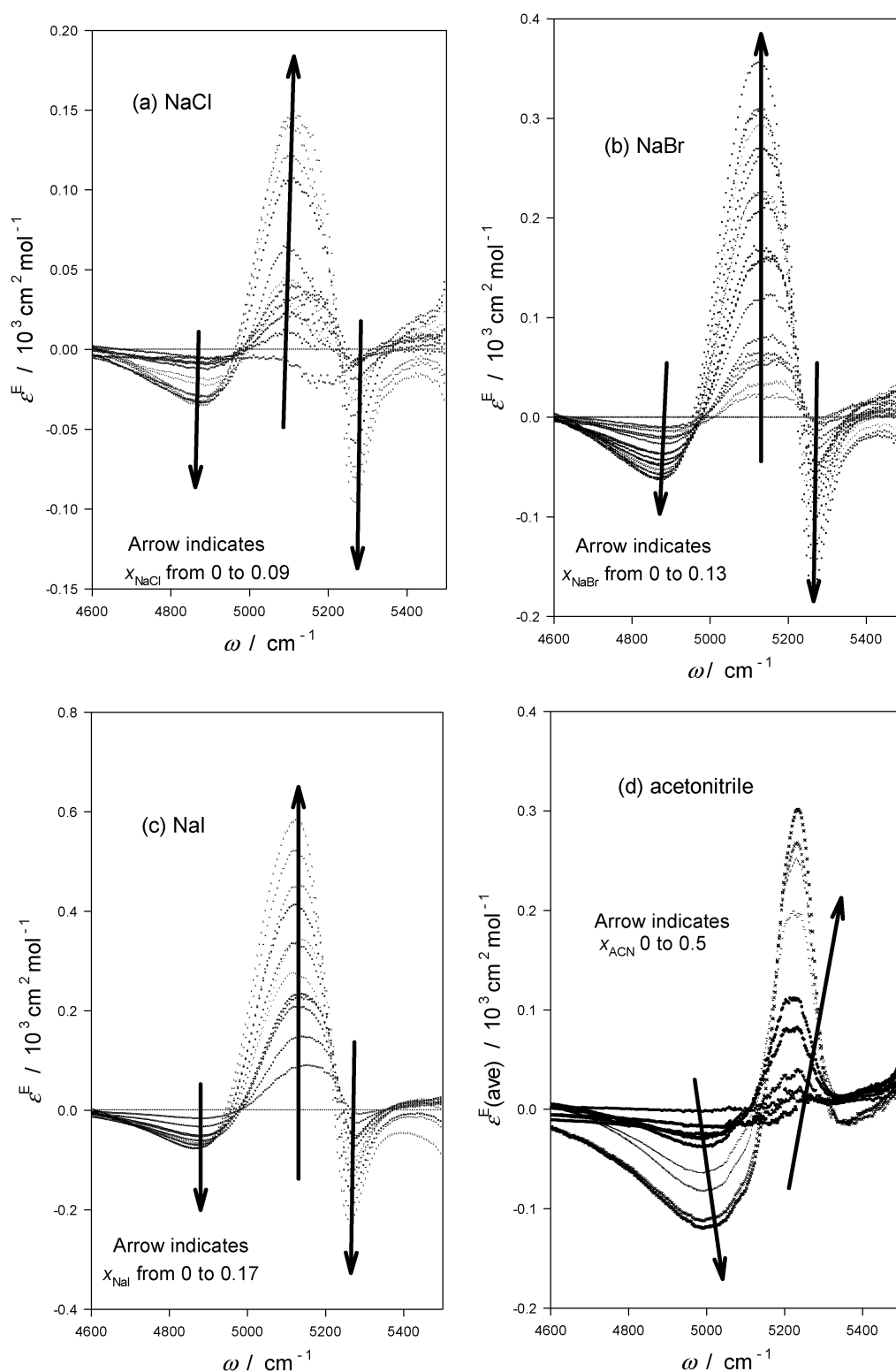
Fig. 2 (a) Excess molar absorptivity, ε^E, for NaCl. (b) Excess molar absorptivity, ε^E, for NaBr. (c) Excess molar absorptivity, ε^E, for NaI. (d) Excess molar absorptivity, ε^E, for acetonitrile.

shown in Fig. 4(a). Namely, the effects of an additional salt on ε^E slow down rather suddenly at these threshold mole fractions. This hints the onsets of some form of ion association, perhaps H_2O-mediated ion-pairing[45] at the thresholds of about $x_{salt} = 0.032$, 0.036, and 0.040 for NaCl, NaBr and NaI respectively.

Fig. 4(b) shows a qualitative difference in, ε_{salt}^E, the anion's effect on ε^E between Cl^- and (Br^-, I^-) pair in the 5123 cm^{-1} region. For Cl^-, the value of ε_{salt}^E is sizeably smaller than an imaginary curve for Cl^-, the broken line in Fig. 4(b) obtained by smoothly extending the trend shown from I^- to Br^-.
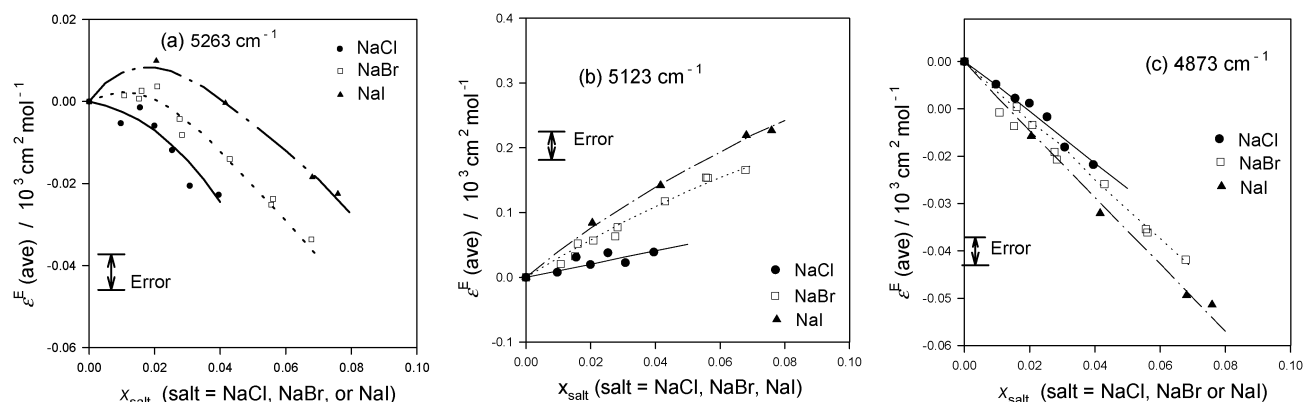
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Phys. Chem. Chem. Phys., 2012, **14**, 4433–4439 | **4437**

Fig. 3 (a) The average excess molar absorptivity, ε^{E}(ave), at 5263 cm^{-1} for aqueous NaCl, NaBr and NaI. (b) The average excess molar absorptivity, ε^{E}(ave), at 5123 cm^{-1} for aqueous NaCl, NaBr and NaI. (c) The average excess molar absorptivity, ε^{E}(ave), at 4873 cm^{-1} for aqueous NaCl, NaBr and NaI.
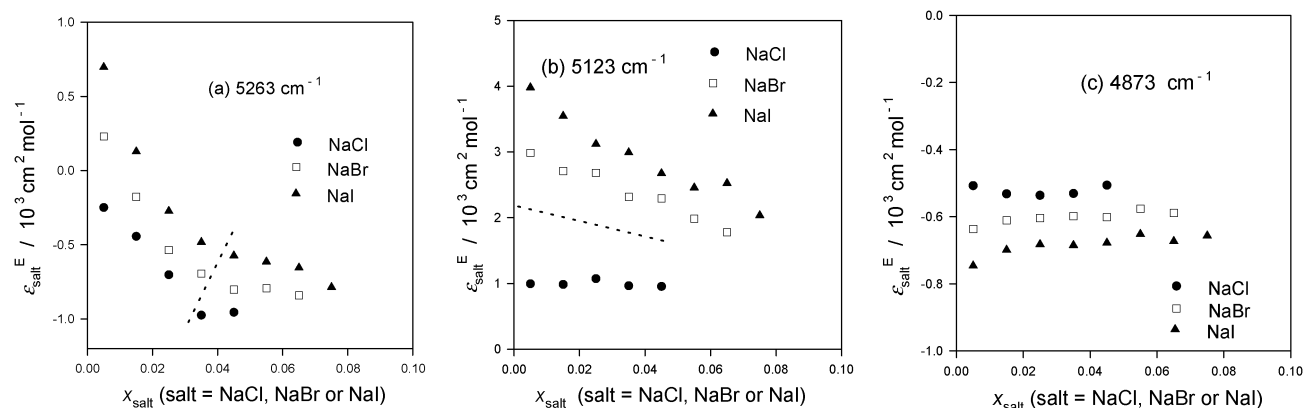

Fig. 4 (a) The excess partial molar absorptivity of salt, $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$, at 5263 cm^{-1} vs. mole fraction of salt, x_{salt}, for aqueous NaCl, NaBr, and NaI. (b) The excess partial molar absorptivity of salt, $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$, at 5123 cm^{-1} vs. mole fraction of salt, x_{salt}, for aqueous NaCl, NaBr, and NaI. (c) The excess partial molar absorptivity of salt, $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$, at 4873 cm^{-1} vs. mole fraction of salt, x_{salt}, for aqueous NaCl, NaBr, and NaI.

Furthermore, the values of $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$ for Cl$^-$ appear constant, while those of Br$^-$ and I$^-$ show a weak decrease on increasing x_{salt}. This may reflect our earlier finding that Cl$^-$, while being hydrated, leaves the bulk H$_2$O away from the hydration shell unperturbed and that Br$^-$ and I$^-$ retard the degree of fluctuation more strongly for I$^-$ than Br$^-$.[18b,24] We thus suggest that $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$, the effect of Na-halides on ε^{E}, at 5123 cm^{-1} is related to the effect of ion on retarding the degree of fluctuation of the mixture. Or rather, the qualitative difference in the anion's effect on the H$_2$O hydrogen bond network between Cl$^-$ and (Br$^-$, I$^-$) manifests itself in the 5123 cm^{-1} vibrational chromophore. For Br$^-$ and I$^-$, as x_{salt} increases, $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$ decreases weakly. If the present interpretation that $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$ at this ω region reflects the ion's power of retarding the degree of fluctuation, the present NIR study indicates that the power of retardation decreases gradually on increasing x_{salt}, while our thermodynamic studies could not reveal such an x_{salt} dependence.

At 4873 cm^{-1} in Fig. 4(c), corresponding to the ice-like degree of hydrogen bonding, a small difference in curvature could be detected between Cl$^-$ and (Br$^-$, I$^-$) in the x_{salt} dependences of $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$. Such conclusion could be still premature, however, judging from the scatters in Fig. 3(c), from which Fig. 4(c) was constructed. Nevertheless, $\varepsilon^{\mathrm{E}}_{\mathrm{salt}}$, the effect of each

ion for decreasing ε^{E} is in the reverse order of charge density of anions. Thus, the effect is not directly coming from the charge but by some more complex effect on the ice-like portion of the $\nu_2 + \nu_3$ band of H$_2$O. A theoretical work on the effect of halide ions on ice-like H$_2$O is also awaited.

We conclude that the qualitative difference of the effect of a halide ion on H$_2$O between Cl$^-$ and (Br$^-$, I$^-$) found by our thermodynamic studies[18b,24] manifests itself in the 5123 cm^{-1} vibrational chromophore, which represents liquid like hydrogen bonding. Further investigation on this ω-region of the $\nu_2 + \nu_3$ band could help elucidate the nature of the effect of halide ions on the molecular organization of H$_2$O.

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