ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理
Chinese Physics B

A universal characteristic water content of aqueous solutions

Xiao Huang(黄晓), Ze-Xian Cao(曹则贤), Qiang Wang(王强)

Citation: Chin. Phys. B . 2019, 28(6): 065101. **doi:** 10.1088/1674-1056/28/6/065101
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Accurate quantification of hydration number for polyethylene glycol molecules

Wei Guo(郭伟), Lishan Zhao(赵立山), Xin Gao(高欣), Zexian Cao(曹则贤), Qiang Wang(王强)

Chin. Phys. B . 2018, 27(5): 055101. **doi:** 10.1088/1674-1056/27/5/055101

Equation of state for warm dense lithium: A first principles investigation

Feiyun Long(龙飞沄), Haitao Liu(刘海涛), Dafang Li(李大芳), Jun Yan(颜君)

Chin. Phys. B . 2017, 26(6): 065101. **doi:** 10.1088/1674-1056/26/6/065101

Recrystallization of freezable bound water in aqueous solutions of medium concentrations

Lishan Zhao(赵立山), Liqing Pan(潘礼庆), Ailing Ji(纪爱玲), Zexian Cao(曹则贤), Qiang Wang(王强)

Chin. Phys. B . 2016, 25(7): 075101. **doi:** 10.1088/1674-1056/25/7/075101

Thermodynamic study of fluid in terms of equation of state containing physical parameters

S. B. Khasare

Chin. Phys. B . 2015, 24(1): 015101. **doi:** 10.1088/1674-1056/24/1/015101

Modified 2CLJDQP model and the second virial coefficients for linear molecules

Zhang Ying, Wang Sheng, He Mao-Gang

Chin. Phys. B . 2014, 23(12): 125101. **doi:** 10.1088/1674-1056/23/12/125101

RAPID COMMUNICATION

The universal characteristic water content of aqueous solutions*

Xiao Huang(黄晓)[1,2], Ze-Xian Cao(曹则贤)[1,2,3], and Qiang Wang(王强)[1,†]

[1] *Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*
[2] *University of Chinese Academy of Sciences, Beijing* 100190, *China*
[3] *Songshan Lake Materials Laboratory, Dongguan* 523808, *China*

(Received 7 March 2019; revised manuscript received 22 March 2019; published online 8 May 2019)

Raman measurements at room temperature reveal a characteristic concentration for a series of aqueous solutions of electrolytes, through which O–H stretching vibration of H_2O or dilute HDO obviously changes their concentration dependence. This characteristic concentration is very consistent with another, through which the solutions undergo an abrupt change in their glass-forming ability. Interestingly, the molar ratio of water to solute at these two consistent concentration points is almost solute-type independent and about twice the hydration number of solutes. We suggest that just when the concentration increases above this characteristic concentration, bulk-like free water disappears in aqueous solutions and all water molecules among closely-packed hydrated solutes exhibit the characteristics of confined water.

Keywords: aqueous solutions, stretching vibration of water, concentration dependence, hydration number

PACS: 51.30.+i, 64.70.D–, 65.20.–w **DOI:** 10.1088/1674-1056/28/6/065101

1. Introduction

Identifying the types of water and quantifying their fractions in aqueous solutions can help us to understand their physiochemical properties and behaviors.[1–9] To achieve this goal, the first challenge is to quantify hydration water. Accordingly, various technological methods with different spatial and temporal resolutions have been adopted to quantify the hydration number of solute, n_h. Regretfully, most of the reported values differ from each other. Recently, following our previous work in the past few years, the universal concentration dependence of the icing/vitrification behavior for aqueous solutions has been established,[10–13] from which a convenient and reliable method of determining n_h is developed.

The value of n_h, quantified based on concentration-dependent crystallization and vitrification of water, reflects the degree of solutes affecting their adjacent water from the viewpoint of promoting solvent water vitrification in a dilute solution. These defined hydration water can easily vitrify at a moderate and even slow rate, *e.g.*, as low as 10^{-2} K/s.[14] The critical cooling rate required for initiating vitrification of bulk water is about 10^6 K/s.[15] For the dilute solution, it can be simply regarded as a mixture of hydrated solute and bulk-like free water. However, with a decrease of water content, more hydration shells become closely compacted and even overlapped and, finally, free water disappears.[5] The question here is whether or not there is an obvious critical concentration point, through which a mixture of hydrated solutes and free water for dilute solutions changes into that of hydrated solutes and confined water for medium-concentrated ones.

As recently reported, for a series of solutions of electrolytes and organic molecules, their glass-forming ability shows an abrupt change at a critical concentration point, defined as $M \cdot n_cH_2O$ for brevity, where M is solute.[10,13] For $M \cdot nH_2O$ with $n > n_c$, some water molecules can easily crystallize into ice upon cooling, even at a high rate. After that, the residual freeze-concentrated solution, which shows high glass-forming ability, can easily vitrify even at a slow cooling rate. In contrast, when water content decreases below that of $M \cdot n_cH_2O$, the solutions can easily vitrify totally. Most interestingly, as already confirmed, the value of n_c/n_h is nearly solute-type-independent for electrolytes and molecules especially with higher molar weights, and $n_c/n_h \approx 1.7$.[12]

Besides glass forming ability, many other properties of water and solute of organic molecule solutions, which are measured at room temperature, also manifest a deflection feature or abrupt change of their concentration dependence with the variation of water content.[16–19] On the side of solvent water, these properties include spin-spin and spin-lattice relaxations,[20] adiabatic compressibility coefficient,[21] diffusion coefficient,[22] viscosity,[19] partial molar volume or vapor pressure,[23] Raman shift, *etc*. On the side of organic molecules solute, the property mainly refers to the CH-stretching vibration.[24] Due to the lack of a clear physical picture behind this behavior, the molar ratio of water to solute at such a deflection point for concentration dependence of phys-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11474325, 11474335, and 51172272), the Fund from the Chinese Academy of Sciences (Grant No. 1731300500030), and the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB07030100).

†Corresponding author. E-mail: qwang@iphy.ac.cn

© 2019 Chinese Physical Society and IOP Publishing Ltd

ical properties has often been taken as the hydration number. Actually, in most cases, the concentration of this deflection point is consistent with that of $M \cdot n_c H_2O$.[24]

Here, we focus our interest on concentration dependence of O–H stretching vibration of water in solutions of electrolytes at room temperature. We find that, like those scenarios observed in solutions of organic molecules, the O–H stretching vibration of water in solutions of electrolytes also displays obviously a deflection at a characteristic concentration, which, most importantly, is also very consistent with that of $M \cdot n_c H_2O$, and $n_c \approx 1.7 n_h$. Therefore, a universal characteristic water content of aqueous solutions highly correlated with the hydration numbers of solutes for properties measured at low and room temperatures is experimentally confirmed.

2. Experiment

2.1. Samples

High-purity water was prepared by using a Millipore Milli-Q system. The salts $CaCl_2$ ($CaCl_2{\cdot}2H_2O$, purity 99.99%), $CaBr_2$ (99.98%), $Ca(NO_3)_2$ (99.99%), $Ca(ClO_4)_2$ ($Ca(ClO_4)_2{\cdot}4\ H_2O$ 99%), $MgCl_2$ (anhydrous 99.99%), $MgBr_2$ (99.99%), $Mg(NO_3)_2$, $Mg(ClO_4)_2$ ($Mg(ClO_4)_2{\cdot}6\ H_2O$ 99%), $AlCl_3$ ($AlCl_3{\cdot}6\ H_2O$ 99%), $Al(NO_3)_2$ ($AlCl_3{\cdot}6\ H_2O$ 99%), and $Al(ClO_4)_3$ ($Al(ClO_4)_3{\cdot}9\ H_2O$ 98%) and D_2O (99.9%) were purchased from Sigma-Aldrich.

2.2. Raman spectrometric measurements

Raman spectra were measured at 295 K by using a Jobin–Yvon HR800 Raman system. For excitation, the spectral line at 532 nm of a laser with about 100 mW was used. The laser power of 1 mW was focused on the sample surface through the fused SiO_2 film with a $\times 50$ long focus objective.

3. Results and discussion

As an example, figure 1 shows the Raman spectra in a range from 2800 cm^{-1} to 3800 cm^{-1} for solutions of $MgCl_2$ of various concentrations measured at 295 K. We choose pure H_2O and mixture of H_2O with D_2O in a molar ratio of $H_2O{:}D_2O = 1:4$, respectively, as a solvent.

In Figs. 1(a) and 1(b), the solution of D_2O for the electrolytes usually has an unaltered hydration number. In Fig. 1(b), the coupling of the OH-stretching vibration, both intramolecular and intermolecular, can be effectively suppressed, and thus improves the accuracy of the peak position at around 3400 cm^{-1} from the Raman spectra. Figure 1(c) shows the plots of the locations of the peak maximum of Raman spectra plotted in Figs. 1(a) and 1(b), and those reported in Ref. [25] *versus* n for $MgCl_2 \cdot nH_2O$ or $MgCl_2$ dissolved in D_2O with dilute H_2O with a molar ratio of 4:1. The variation of peak position for the component around 3400 cm^{-1} obtained by Gaussian fitting of the spectra in Fig. 1(a), as conventionally done in the literature, is also presented for comparison. Clearly, in all the cases, the peak position of the OH-stretching vibration shows a deflection point, a change of tendency, in their water-content dependence. Noticeably, the deflection occurs at $n \approx 20$, corresponding to $n_c \approx 1.7 n_h$ ($n_h = 12$[13]).

The deflection behavior of the water content dependence of peak position of Raman spectra shown in Fig. 1(c) can be verified in aqueous solutions of various other electrolytes (Fig. 2), where the peak positions of Raman spectra for the OH-stretching vibration, measured at 295 K, are plotted as a function of n/n_h. As determined previously, n_h ranges from 6 for LiCl to 19 for $AlCl_3$.[13] Over such a wide range of n_h, the water content dependence of the Raman shift measured on these aqueous solutions inclusively displays a deflection point at $n/n_h. \approx 1.7$. All of these electrolyte solutions also show similar water content dependence of icing/vitrification of water to the behavior shown in Fig. 1(d). For more details, see Supplementary Information of Ref. [13].

The deflection occurring at $M \cdot n_c H_2O$, where $n_c \approx 1.7 n_h$, may be related to the variation of microstructure of water and solute in aqueous solution as the concentration changes. As mentioned earlier, the solvent water may be found to be in different status, namely free water, confined water (spatially confined among hydrated solutes), and hydration water, respectively, depending on the water content. To explain the abrupt change in glass forming ability of aqueous solutions at $M \cdot n_c H_2O$ as shown in Fig. 1(d), we have recently suggested that aqueous solutions can be divided into three distinct concentration zones (Fig. 1(d)). Solutions within water-rich zone III, solvent water is comprised of hydration water and bulk-like free water. Free water can easily crystallize into ice, and, differently, hydration water can easily vitrify. The value of n_h is then quantified just based on this characteristic feature of hydration water. When water content decreases below $M \cdot n_c H_2O$, the aqueous solutions can easily vitrify, even at a slow cooling rate. It has been suggested that this abrupt change in glass forming ability of solution can be mainly attributed to the disappearance of free water. In other words, solutions change from a mixture of free water and hydrated solutes within zone III to a mixture of hydrated solutes and confined water in zone II. This proposition can be proved by the cold-crystallization behavior of water appearing upon thawing vitrified or deeply supercooled aqueous solutions at concentrations within zone II. Otherwise, if all water molecules in zone II are regarded as hydration water, then solutions within this zone show only devitrification behavior in heating process, such as that of the solutions within zone I, wherein solutes cannot be hydrated to the greatest extent.

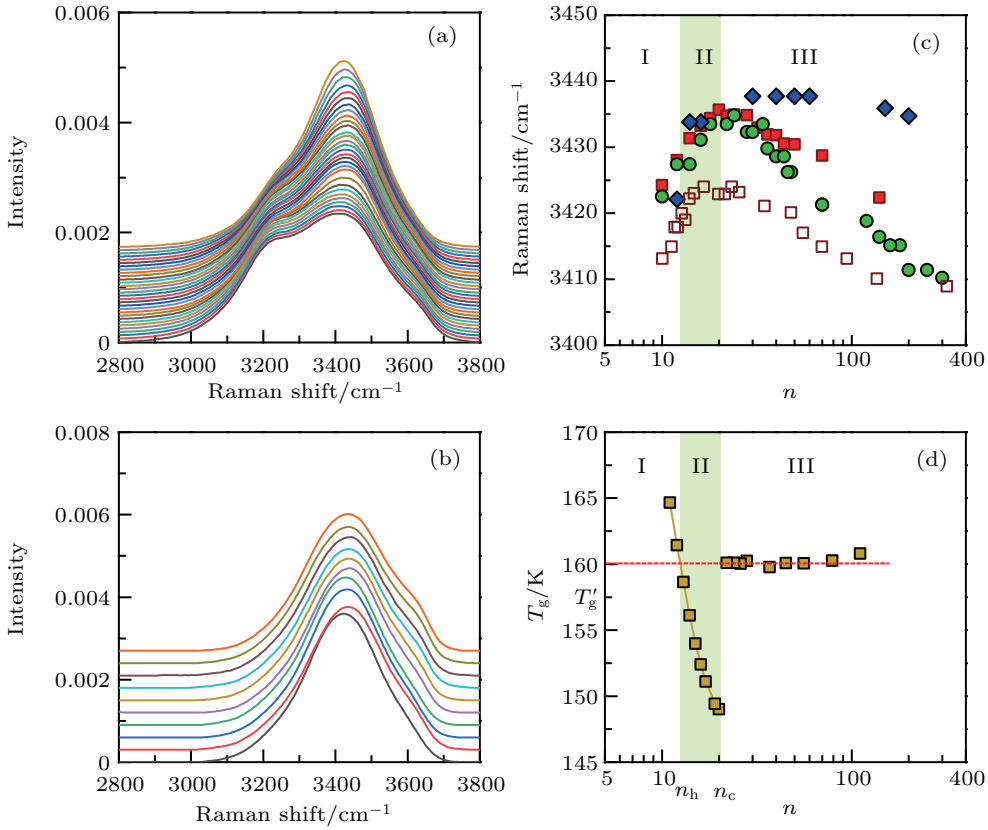


Fig. 1. (a) Raman spectra for OH-stretching vibration of H_2O for $MgCl_2$ solutions, $MgCl_2 \cdot nH_2O$, with $n = 300$, 200–80 in steps of 20, and 50–10 in steps of 2 (from bottom curve to top curve). (b) OH-stretching vibration of HDO in solution of $MgCl_2$ dissolved in D_2O mixed with dilute H_2O with a molar ratio of 4:1. Molar ratios of water to solute n are 200 (bottom curve), 150, 60, 50, 40, 30, 26, 16, 14, 12 (top curve). (c) Peak position for OH-stretching vibration as a function of n plotted on the basis of data from panels (a) (solid circle) and (b) (solid diamond). The data of $MgCl_2 \cdot nH_2O$ reported by Burikov *et al.*[25] are also shown for comparison (empty square). Moreover, the peak position of the component around 3400 cm^{-1} obtained by Gaussian fitting of the spectra in panel (a) is also presented (solid square). (d) Water content dependence of glass transition temperatures, T_g, of aqueous solution of $MgCl_2$. In dilute solutions with $n > n_c$, glass transition occurs after spontaneous icing in cooling process, thus it involves only the glass transition of freeze-concentrated solution, which manifests an almost constant T_g, defined as T_g'. The extension of T_g'–n can intersect the fitting curve of T_g–n for concentrated solutions at a feature point, *i.e.*, $MgCl_2 \cdot n_hH_2O$, where n_h is the hydration number of solute. For more details, see Supplementary Information in Ref. [13].

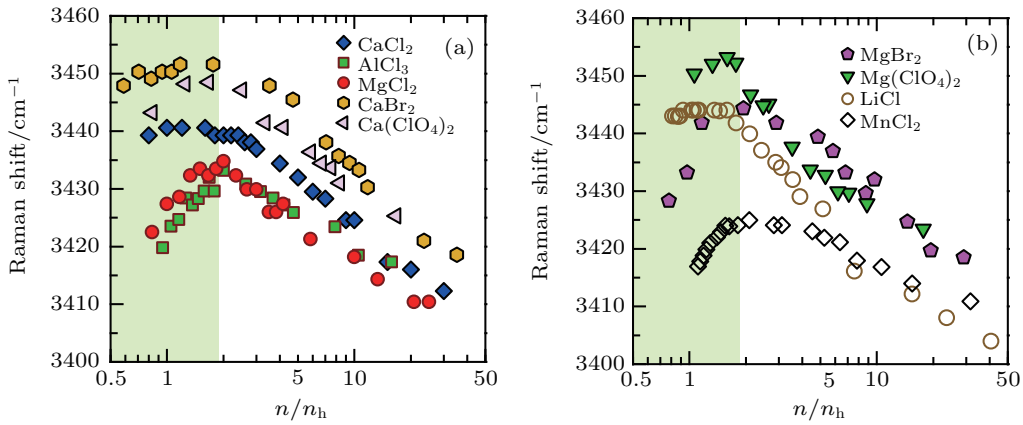


Fig. 2. Peak position of Raman spectra for the OH stretching vibration of water at about 3400 cm^{-1} as a function of the ratio of n/n_h for aqueous solutions of various electrolytes $M \cdot nH_2O$. In panel (a) M refers to $CaCl_2$ (diamond), $CaBr_2$ (hexagon), $Ca(ClO_4)_2$ (triangle), $MgCl_2$ (circle), and $AlCl_3$ (square), and in panel (b) M refers to $MgBr_2$ (pentagon), $Mg(ClO_4)_2$ (triangle), LiCl[25] (circle), and $MnCl_2$[25] (square).

The previously-mentioned division of concentration zone is further confirmed by an obvious change in concentration dependence of OH-stretching vibration of solvent water at $M \cdot n_cH_2O$ as highlighted in this work. Actually, this non-monotonic dependence of OH-stretching vibration of water on concentration has already been tentatively discussed based on a proposed change in the configuration of ion-pairs with water content.[25] With decreasing the water content, the ion-pairs in solution gradually come into contact from the initially isolating status through the solvent-sharing intermediate stage.[26,27]

For some solutes, such as LiCl presented in Fig. 2(b) (empty circles), the ions always tend to stay separated by hydration water due to a strong cation-water interaction and a relatively weak anion-water interaction.[28] In this case, below a critical water content point, the hydration water can be believed to be structurally insensitive to a further increase of solute content. As a result, the peak position of the O–H stretching vibration remains nearly unchanged at low water content. However, in those aqueous solutions with stronger cation-anion interaction, even if solvent-separated or solvent-sharing ion-pairs are present in water-rich environment, the ion-pairs may come into contact with further reducing the water content. If the fraction of contacting ion-pairs increases with reducing water in the water-poor solutions, the water molecules will become more strongly hydrogen-bound to each other. Consequently, the Raman spectra of the solvent water will be red-shifted as the water content is reduced. This explanation in terms of ion-pair configuration above seems to be implacable to water in aqueous solution of CsCl, because the Cs^{+1} and Cl^{-1} ions will come into contact even in a water-rich solution,[28] yet the solution still manifests this deflection feature of the water content dependence of the OH-stretching vibration.[25] Therefore, the detailed mechanism obtained from the microstructures of the solution needs further investigation.

4. Conclusions

In this work, we have measured the Raman spectra of the O–H stretching vibration of water for aqueous solutions of a series of electrolytes in a wide range of water content. The results clearly exhibit a deflection point, which appears inclusively at the water content corresponding to $n_c \approx 1.7n_h$, where n_h represents the hydration number of the given solute. The existence of the critical hydration number n_c, together with n_h which divides the aqueous solution into three distinct zones, is studied in the investigation of low temperature behaviors such as icing/vitrification. The critical hydration number n_c indicates a turning tendency for the variation of microstructures in the aqueous solution, and it is reasonable that it will exhibit some properties of the solutions at room temperature. This characteristic feature is universal for solutions of organic molecules and even of electrolytes, and it might help us to understand the bizarre variation tendency of properties of aqueous solutions, particularly those with water content in the neighborhood specified by the critical hydration number.

References

[1] Bellissent-Funel M C, Hassanali A, Havenith M, Henchman R, Pohl P, Sterpone F, van der Spoel D, Xu Y and Garcia A E 2016 *Chem. Rev.* **116** 7673
[2] Laage D, Elsaesser T and Hynes J T 2017 *Chem. Rev.* **117** 10694
[3] Perticaroli S, Ehlers G, Stanley C B, Mamontov E, O'Neill H, Zhang Q, Cheng X L, Myles D A A, Katsaras J and Nickels J D 2017 *J. Am. Chem. Soc.* **139** 1098
[4] Burakowski A and Glinski J 2012 *Chem. Rev.* **112** 2059
[5] Marcus Y 2009 *Chem. Rev.* **109** 1346
[6] Gliński J and Burakowski A 2008 *Eur. Phys. J.-Spec. Top.* **154** 275
[7] Burakowski A and Gliński J 2007 *Chem. Phys.* **332** 336
[8] Wolfe J, Bryant G and Koster K L 2002 *Cryo-Lett.* **23** 157
[9] Ohtaki H and Radnai T 1993 *Chem. Rev.* **93** 1157
[10] Zhao L S, Cao Z X and Wang Q 2015 *Sci. Rep.* **5** 15714
[11] Zhao L S, Pan L Q, Ji A L, Cao Z X and Wwang Q 2016 *Chin. Phys. B* **25** 075101
[12] Zhao L S, Pan L Q, Cao Z X and Wang Q 2016 *J. Phys. Chem. B* **120** 13112
[13] Wang Q, Zhao L S, Li C X and Cao Z X 2016 *Sci. Rep.* **6** 26831
[14] Angell C A 2002 *Chem. Rev.* **102** 2627
[15] Sosso G C, Chen J, Cox S J, Fitzner M, Pedevilla P, Zen A and Michaelides A 2016 *Chem. Rev.* **116** 7078
[16] Shikata T, Takahashi R and Sakamoto A 2006 *J. Phys. Chem. B* **110** 8941
[17] Branca C, Magazu S, Maisano G, Migliardo F, Migliardo P and Romeo G 2002 *J. Phys. Chem. B* **106** 10272
[18] Liu K J and Parsons J L 1969 *Macromolecules* **2** 529
[19] Jora M Z, Cardoso M V and Sabadini E 2016 *J. Mol. Liq.* **222** 94
[20] Lüsse S and Arnold K 1996 *Macromolecules* **29** 4251
[21] Pochylski M, Aliotta F, Blaszczak Z and Gapiński J 2006 *J. Phys. Chem. B* **110** 20533
[22] Borodin O, Trouw F, Bedrov D and Smith G D 2002 *J. Phys. Chem. B* **106** 5184
[23] Kushare S, Terdale S, Dagade D and Patil K 2007 *J. Chem. Thermodyn.* **39** 1125
[24] Guo W, Zhao L S, Gao X, Cao Z X and Wang Q 2018 *Chin. Phys. B* **27** 055101
[25] Burikov S A, Dolenko T A and Fadeev V V 2007 *Proc. SPIE* **6733** 67330G
[26] van der Vegt N F A, Haldrup K, Roke S, Zheng J R, Lund M and Bakker H J 2016 *Chem. Rev.* **116** 7626
[27] Marcus Y and Hefter G 2006 *Chem. Rev.* **106** 4585
[28] Collins K D, Neilson G W and Enderby J E 2007 *Biophys. Chem.* **128** 95