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Accurate quantification of hydration number for polyethylene glycol molecules*

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Hydration water can even decide the physicochemical properties of hydrated organic molecules. However, by far the most important hydration number for organic molecules, in particular polyethylene glycol which we are concerned with here, usually suffers from a large discrepancy. Here, we provide a scheme for accurate and unambiguous quantification of the hydration number based on the universal water-content dependence of glass transition temperature for aqueous solutions, testified by experimental results for polyethylene glycol molecules of a molar weight ranging from 200 to 20000. Moreover, we also clarify the fundamental misunderstanding lying in the definition and quantification of hydration water for PEG molecules in the literature, therein the hydration number for PEG in water-rich solutions has been determined at a critical concentration, across which the properties of the solution display obviously distinct water-content dependence.

Keywords: hydration number, aqueous solution, polyethylene glycol, vitrification and crystallization

PACS: 51.30.+i, 64.70.D–, 65.20.–w **DOI:** 10.1088/1674-1056/27/5/055101

1. Introduction

Polyethylene glycol (PEG), a precipitant of purifying proteins, has been widely investigated also for its important applications in biopharmaceutical and biomedical industries in addition to its capability of approximately simulating the folding/unfolding of protein. All the processes mentioned above usually undergo in an aqueous environment,[1–8] wherein the interaction between PEG and water often plays a decisive role. This interaction can be effectively described by hydration number n_h and the strength of interaction between hydration water and PEG molecule. A particular PEG molecule is specified with the formula H–[O–CH_2–CH_2]$_n$–OH, where n is referred to as the number of PEG units. So far, hydration numbers for various PEG molecules have been obtained on the basis of a variety of distinct experimental technologies, including nuclear magnetic resonance (NMR),[9–12] Raman scattering,[13] Brillion scattering,[14–16] quasi-elastic neutron scattering,[17–20] broadband dielectric spectroscopy,[21–23] differential scanning calorimetry (DSC),[24–35] and of measurements of different properties such as the compressibility coefficient,[36,37] vapor pressure,[38,39] and viscosity.[40,41] Also the molecular dynamics simulation contributed some to this enterprise.[42] However, the reported values of hydration number per PEG unit scattered between 1 and 4, suffering from an intolerable discrepancy.

Recently, our research group (Wang & Cao) developed a method for determining n_h of electrolytes and small organic molecules in their corresponding water-rich solutions, i.e., solutions falling in zone III, based on a universal feature of water-content dependence of vitrification and crystallization behaviors of water in solutions.[43] In brief, the solute-rich aqueous solutions can easily vitrify even when cooling at a moderate rate, e.g., of 20 K/min., and the glass transition temperature of solution, T_g, decreases monotonically with increasing water content due to the plasticizer effect of water. With further increasing of water content beyond a critical point, denoted by X^c_{aqu}, ice precipitation occurs first in the cooling process, followed by the vitrification of the freeze-concentrated phase, which certainly manifests a constant glass transition temperature, now denoted by T'_g. The content of water in the freeze-concentrated phase thus provides an unambiguous and pertinent definition of hydration water. It can be directly read from the monotonous part of the T_g versus water content curve at the point where $T'_g = T_g$. This method has been justified by applying to the aqueous solutions of various mixed solutes.[44]

The current work is devoted to justifying the aforementioned method for determining the hydration number of organic molecules with a large molecular weight, e.g., PEG with a molecular weight up to 20000. In addition, more importantly, it is found that the molar ratio of water to solute at X^c_{aqu} exactly corresponds to the upper limit of the reported n_h values for PEG. In PEG solutions with a water content below and above X^c_{aqu}, water displays obviously distinct vitrification and crystallization behaviors. Such a sudden change with the water content in the neighborhood of X^c_{aqu} can also be observed in many features of PEG aqueous solutions. That the corre-

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sponding number of water at this critical concentration has been widely taken as the hydration number arises from a misunderstanding. In fact, at X^{c}_{aqu} water in the solution includes both the hydrated water and those confined among the hydration spheres of solutes.

2. Experimental details

Aqueous solutions of PEG with a molecular weight ranging from 200 g/mol to 20000 g/mol were prepared with Millipore water and high-purity solutes (Sigma-Aldrich). DSC measurements were performed on a calorimeter (Perkin Elmer DSC8000) at a cooling/heating rate of 20 K/min. When cooled down to 123 K, the samples were held at that temperature for 1 min before performing the subsequent heating procedure. Here, T_g was extracted from the onset point of the heating curve, following the conventional scheme for determining the glass transition temperature. Raman spectra were measured on a confocal microscope/Raman spectrometer system (Jobin-Yvon HR800) with the 532 nm diode laser excitation. A laser beam of 1 mW in power was focused onto the sample surface through a 0.3 mm-thick fused SiO_2 plate. The integration time was set at 40 ms per point with a spectral resolution of 0.5 cm^{-1}.

3. Results and discussion

Figure 1 displays the water-content dependence of vitrification and crystallization behaviors for the aqueous solutions of PEG 20000. Similar to the observation in a series of aqueous solutions of electrolytes and small organic molecules,[43–45] the solute-rich solutions of PEG 20000 vitrify neatly (Fig. 1(a)): the DSC curve looks quite simple. But, when cooling the water-rich samples, water crystallization occurs first, followed by vitrification of the freeze-concentrated phases (Fig. 1(b)), which, as expected, manifests an almost constant glass transition temperature, as denoted by T'_g in Fig. 1(c). The freeze-concentrated phase corresponds to the solution that totally vitrifies at $T_g = T'_g$, thus of which the water content can be directly read from the monotonous part of the T_g versus X_{aqu} curve. The water fraction for the solution thus is determined and denoted as X'_{aqu}. The hydration number for PEG 20000 calculated from X'_{aqu} is 1.6 per PEG repeat unit. For other PEG molecules, i.e., PEG 200, 300, 400, 600, 1000, 2000, 3000, 4000, 6000, and 10000, the hydration number n_h obtained from this quantification scheme is plotted in Fig. 2(a) as a function of the number of PEG units, n. One sees that n_h increases steadily from 1 for PEG 200 up to about 1.6 for PEG 20000.

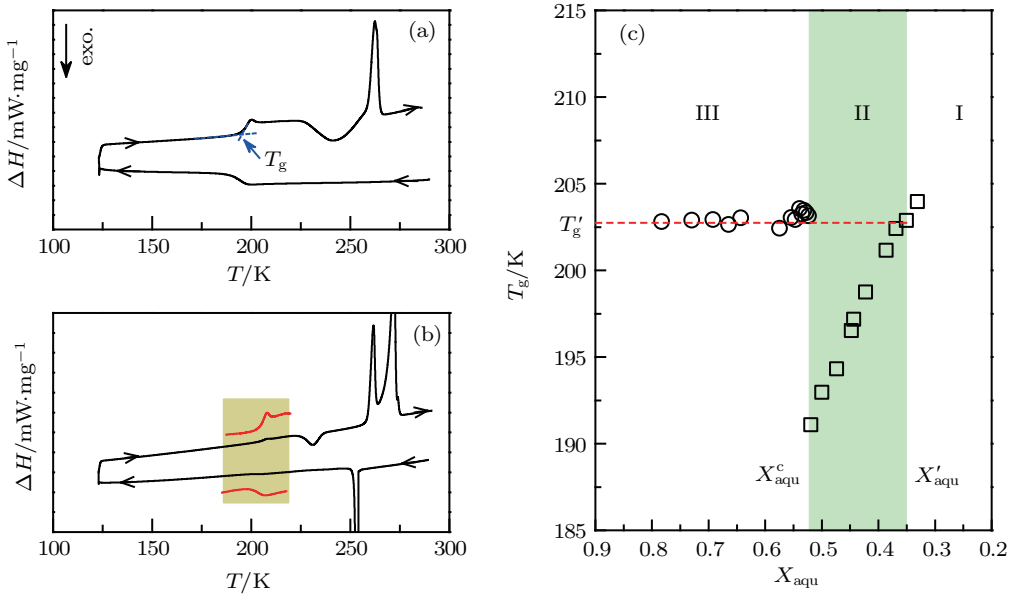


Fig. 1. (color online) (a) DSC thermograms of aqueous solutions of PEG 20000 with a mass fraction of water of (a) $X_{aqu} = 0.47$, and (b) $X_{aqu} = 0.78$. Water in the high-concentration solution (a) vitrifies easily upon cooling, and upon the subsequent reheating the devitrified solution, a portion of water cold-crystallizes into ice (exothermic peak) which then melts upon further heating (endothermic peak). In the water-rich solution (b), water directly crystallizes into ice upon cooling, followed by vitrification of the freeze-concentrated phase. Upon subsequent reheating, the devitrified freeze-concentrated phase undergoes cold-crystallization first and then melts with further increasing temperature. Ice precipitated upon the cooling process melts at a comparatively higher temperature. (c) Water content dependence of glass transition temperature T_g for the high-concentration solutions (square) and for the freeze-concentrated phase (circle) resulting from icing of the water-rich solutions, respectively. At X'_{aqu}, $T_g = T'_g$, i.e., the glass transition temperature for the free-concentrated phase.

As shown in Fig. 1(c), there is a critical point in the water-content dependence of T_g, i.e., X^{c}_{aqu}. At X^{c}_{aqu}, the average number of water per PEG unit, here denoted as n_{cr}, is roughly 2.6 for all the PEG molecules concerned here, see Fig. 2(b). Water in the solutions manifests distinct vitrification and crystallization behaviors during the cooling process even at the same rate, depending on whether the water content is above or below X^{c}_{aqu}. As already settled in a previous in-

vestigation, for electrolytes, n_{cr} is strongly related to n_h, and it has $n_{cr}/n_h = 1.7$,[44] insensitive to the type of electrolytes although it involves mono-, bi-, and trivalent cations. For comparison, the ratio n_{cr}/n_h for PEG is also plotted in Fig. 2(c) as a function of the number of PEG units, n. Clearly, n_{cr}/n_h decreases from about 2.6 for PEG 200 to about 1.7 for PEG 20000. In other words, for PEG 20000 ($n = 454$), the ratio of n_{cr}/n_h approaches the value for electrolytes. This observation can be reasonably understood if the entangled hydrated PEG 20000 has an approximately spherical symmetry to the hydrated ions. A further discussion about this observation is beyond the scope of the current article. Here, we only want to emphasize the fact that water in aqueous solutions manifests obviously distinct different vitrification or crystallization behaviors when the water content in the solution varies across X^c_{aqu}.

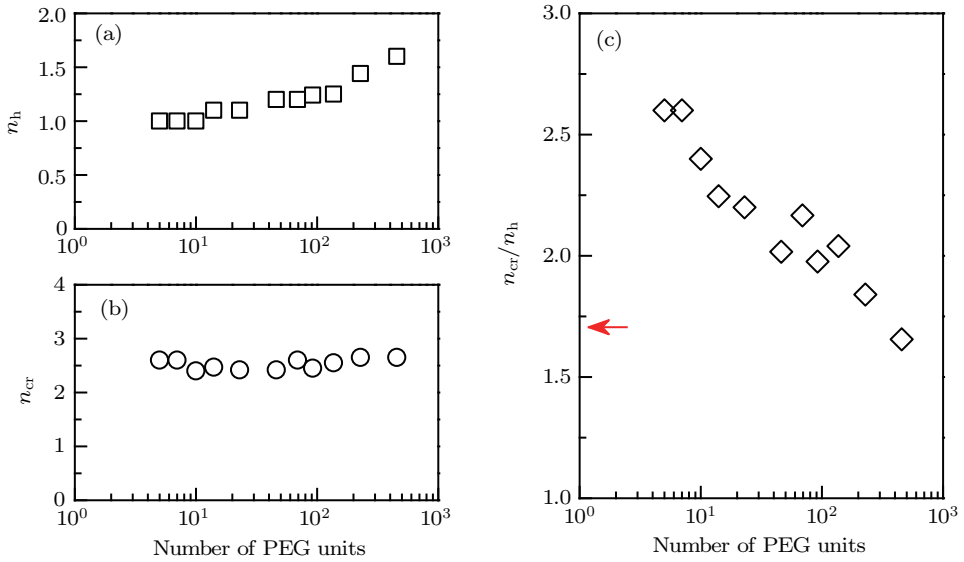


Fig. 2. (color online) (a) Hydration number n_h, (b) critical hydration number n_{cr}, and (c) n_{cr}/n_h for PEG molecules as a function of the number of PEG units. The arrow indicates $n_{cr}/n_h = 1.7$ for electrolytes.

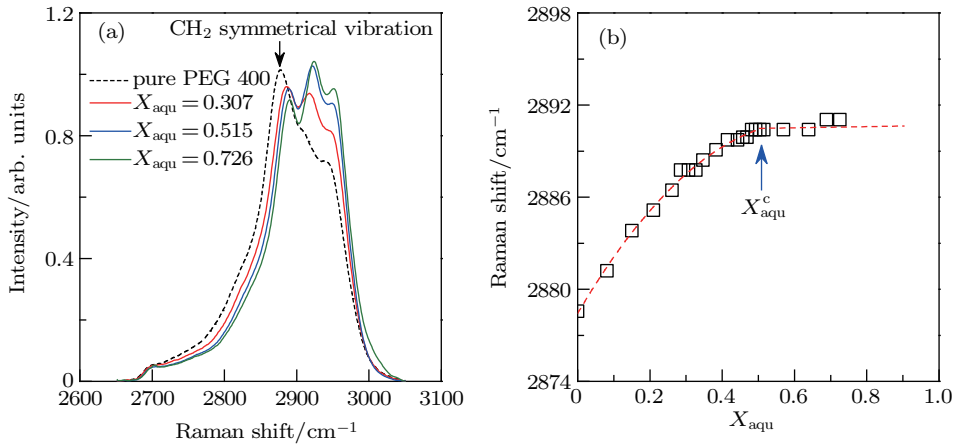


Fig. 3. (color online) (a) Raman spectra of aqueous solutions of PEG 400 with different mass fractions of water. (b) Water content dependence of the peak position of the symmetrical stretching mode of CH_2 in the PEG 400 molecule. The arrow in panel (b) indicates X^c_{aqu} labeled in Fig. 1(b).

When the water content in the solution varies across X^c_{aqu}, the symmetric stretching vibration of CH_2 blocks in PEG molecules also reveals a sudden change in its water-content dependence. For instance, figure 3(a) shows the Raman spectra of PEG 400 solutions with different water contents measured at room temperature. The peak around 2878 cm^{-1} corresponds to the symmetric stretching vibration of CH_2 in the PEG chain.[46–48] With the addition of more water, this Raman mode continuously shifts from 2878 cm^{-1} at $X_{aqu} = 0$ to about 2890 cm^{-1} at X^c_{aqu}, from there on it stands still despite the further increasing of water, see Fig. 3(b). The same behavior can also be observed in aqueous solutions of other PEG molecules.

We shall put forward a more clear picture concerning the relationship between X^c_{aqu} and X'_{aqu}, to justify which of n_{cr} and n_h can be regarded as the hydration number in water-rich solutions. As shown in Fig. 1(c), the aqueous solutions can be categorized into three distinct zones with regard to the crystallization and vitrification behaviors of water. For solutions in

zone I, there is only bound water, or speaking more strictly, non-freezable bound water. These water molecules are directly bound to the solutes, showing a strong glass-forming tendency and are very difficult to crystallize upon cooling and reheating. With the addition of more water, the solutions fall in zone II, in which some excess water molecules are confined in the space among the hydration spheres of the solutes. These confined water molecules are normally regarded as freezable bound water,[49] i.e., they can easily turn vitrified together with the hydration spheres upon cooling, but they crystallize into ice during the reheating process, a phenomenon referred to as cold crystallization. They can also crystallize into ice after a long-time isothermal holding under a supercooled state. The solutions in zone III contain some free water molecules that will eventually constitute the main component of the water-rich solutions. Free water is less affected by the presence of hydrated solutes and can easily crystallize into ice during the cooling process. As the confining condition for some water, as is the case in solutions of zone II, is now released, there is then no more freezable bound water. The difference between n_{cr} and n_h provides a measure for the quantity of freezable bound water. Whether there exists any freezable bound water is a pivotal factor in determining the water-content dependence of properties for aqueous solutions.

Hence we see that it is unreasonable to take n_{cr} as the hydration number for a solute in water-rich solutions. However, regretfully, such a viewpoint and the relevant quantification scheme have been widely accepted and applied in particular to PEG and other organic molecules. For example, to quantify the hydration numbers of PEG, a variety of properties of PEG solutions have been widely measured to acquire in particular their water-content dependencies, including the proton spin-lattice relaxation time T_1, proton spin-spin relaxation time T_2,[9,10,12] and proton chemical shifts,[11] dielectric relaxation time of water,[21–23] sound velocity,[14–16] diffusion coefficient,[17–20] adiabatic compression coefficient,[36] viscosity,[40,41] and the stretching vibration of C–O–C.[13] Just as the symmetric stretching vibration of CH_2 in PEG shown in Fig. 3(b), most of the above-mentioned properties experience a sudden change when the water content comes across the corresponding X^c_{aqu} (Table 1). This method has also been applied to determine the hydration number for ethanol,[51] cellulosic materials,[52] etc. and the results suffer from the same inadequacy as for PEG here concerned.

Table 1. Comparison of hydration numbers for PEG obtained with different methods.

Solutes	Methods	Properties	n_h[a]	n_h[b]
PEG 2000, 6000, 20000, 200000[9,10,12]	NMR	T_1, T_2		1[9,10,12]
PEG 400[11]	NMR	δ		3[11]
PEG 6000, 3000000[13]	RS	$\Delta\omega$		3[13]
PEG 300, 400, 1500, 3000, 7500[21]	BDS	τ	3.7[21]	
PEG 100, 150, 400, 600[14–16]	BS	υ_s, κ_s		1.8[14–16]
PEG 200, 400, 600, 1000, 2000, 2300, 6000[18–20]	QENS	D	2–5[18]	1,[19] 2.3[20]
PEG 400, 1000, 4000[36,37]		υ_s, κ_s, v_m		2.2–2.4[36,50]
PEG 200, 300, 400, 1000, 1540, 1550, 2000, 4000, 6000, 70000[26–30,33,34]	DSC	ΔH_m	0.9,[34] 2,[27] 2.4,[28] 1.7–3.3,[29,30] 2.7[33]	4[26]
PEG 240, 440, 560, 950, 1400, 3700, 5700, 6000[38,39]		P		3[38,39]
PEG 200, 300, 400, 600, 35000[40,41]		B, η	2–28[40,41]	
PEG 880[42]	MD	PDF	2[42]	
PEG 200, 300, 400, 600, 1000 2000, 3000, 4000, 6000, 10000 20000[this work]	DSC	T_g	1–1.6 [this work]	2.7[this work]
PEG 200, 400, 4000, 10000[this work]	RS	$\Delta\omega$		2.7[this work]

NMR: nuclear magnetic resonance; BS: Brillouin scattering; BDS: broad dielectric spectroscopy; QENS: quasi-elastic neutron scattering; RS: Raman scattering; DSC: differential scanning calorimetry; MD: molecular dynamics simulation; T_1: spin-lattice relaxation time; T_2: spin-spin relaxation time; δ: chemical shift; υ_s: speed of sound; κ_s: adiabatic compressibility coefficient; τ: dielectric relaxation time; D: diffusion coefficient; η: viscosity; B: viscosity coefficient; $\Delta\omega$: Raman shift; v_m: partial molar volume; p: partial vapor pressure; ΔH_m: melting enthalpy; PDF: partial radial distribution function; T_g: glass transition temperature.

n_h[a]: hydration number determined by directly measuring the hydration radius, the amount of non-freezing hydration water, the number of water in the first hydration shell, the dielectric relaxation properties of hydration water in water-rich solutions.

n_h[b]: hydration number obtained at a critical concentration point, at which the properties of the solutions display obviously different water-content dependences.

Finally, a fact must be pointed out that the vitrified freeze-concentrated phases for different solutions often show different cold-crystallization abilities. For example, for solutions of PEG with molar weights from 200 to 20000, within their corresponding zone III (Fig. 1(c)), the freeze-concentrated phases can easily totally vitrify upon the cooling process, similar to those of solutions of electrolytes and other small organic molecules reported previously. However, during the reheating process, for the solutions of PEG molecules with comparatively higher molecular weights, e.g., from 1000 to 20000, a cold-crystallization process always appears upon heating the devitrified freeze-concentrated phase. This behavior is obviously different from that of water-rich solutions of small organic molecules (including PEG molecules with

molecular weights less than 1000) and electrolytes, therein, the devitrified freeze-concentrated phases keep their liquid state upon the whole reheating process.[43,44,49] This cold-crystallization comes from the freeze-concentrated phase but not non-freezable bound water. Otherwise, only one melting process appears on the DSC heating curve because both primarily precipitated ice and cold-crystallized ice must melt at the same temperature. However, as shown in Fig. 1(b), two melting processes can be observed on the heating DSC curve. By far, it is still difficult to explain the cold-crystallization ability of different freeze-concentrated phases and to evaluate its dependence on the interaction strength between non-freezable bound water and solutes. However, a fact is clear that the cold-crystallization ability of the freeze-concentrated phase does not affect the applicability of method shown in Fig. 1(c) for determining the hydration number of solutes. In other words, the method stressed in this work is valid only if the concentrated solutions in zones I and II and the freeze-concentrated phase in zone III (Fig. 1(c)) can totally vitrify during the cooling process.

4. Conclusions

In summary, DSC and Raman spectroscopic measurements were performed to investigate the water-content dependence of vitrification and crystallization behaviors for aqueous solutions of PEG with a molecular weight up to 20000. Similar to aqueous solutions of electrolytes and small organic molecules, solutions of PEG with different molecular weights can also be categorized into three distinct zones. Even for the solutions in the water-rich zone, hydrated water should be defined as those strongly bound to the solute, and vitrify together with the solute in the form of hydration spheres. In the solutions with a water content over a critical value of X^{c}_{aqu}, the confining condition for the freezable bound water is released, and the constant glass transition temperature, T'_g, for water-rich solutions refers to the freezing concentrated phase. Thus the hydration number can be calculated from this freezing concentrated phase, which corresponds to the dense solution, which can easily vitrify totally, that manifests a glass transition temperature of T'_g. This work also clarifies why for dilute aqueous solutions a sudden change occurs in the water-content dependence of a variety of properties. It is improper to take this critical water content as the index of hydration water, since it also contains part of water that can be bound, but is also freezable.

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