

# A novel method for the determination of membrane hydration numbers of cations in conducting polymers

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**Abstract** Polypyrrole polymer films doped with the large, immobile dodecylbenzene sulfonate anions operating in alkali halide aqueous electrolytes has been used as a novel physico-chemical environment to develop a more direct way of obtaining reliable values for the hydration numbers of cations. Simultaneous cyclic voltammetry and electrochemical quartz crystal microbalance technique was used to determine the amount of charge inserted and the total mass change during the reduction process in a polypyrrole film. From these values, the number of water molecules accompanying each cation was evaluated. The number of water molecules entering the polymer during the initial part of the first reduction was found to be constant and independent of the concentration of the electrolyte below ~1 M. This well-defined value can be considered as the primary membrane hydration number of the cation involved in the reduction process. The goal was to investigate both the effects of cation size and of cation charge. The

membrane hydration number values obtained by this simple and direct method for a number of cations are:

$$\begin{aligned} \text{Li}^+ &: 5.5 - 5.3; \text{Na}^+ : 4.5 - 4.3; \text{K}^+ : 2.3 - 2.5; \\ \text{Rb}^+ &: 0.9 - 0.8; \text{Cs}^+ : \sim 0; \text{Mg}^{2+} : 10.4 - 10.6; \\ \text{Ca}^{2+} &: 7.9 - 8.1; \text{Sr}^{2+} : 5.7 - 6.1; \text{Ba}^{2+} : 3.0 - 3.1; \\ \text{Y}^{3+} &: 13.6 - 13.8; \text{La}^{3+} : 9.0 - 9.1. \end{aligned}$$

The hydration number for all of these cations seems to follow the same simple relation.

**Keywords** Polypyrrole · Hydration number · Solvation number · Cyclic voltammetry · EQCM

## Introduction

Hydration is the process of attraction and association of water molecules with ions of an electrolyte salt in an aqueous solution. When an electrolyte salt is dissolved in an aqueous media, the metal ion cannot be considered to be a bare ion in the aqueous phase. A number of water molecules are associated with the metal ion. These water molecules surround the metal ion and their behaviour is affected by the metal ion. Generally, in an aqueous phase containing hydrated ions, a division of the water molecules into three types has become standard: A group of water molecules that are in direct contact and are coordinated to the metal ions are termed the primary hydration shell or inner hydration shell [1, 2]. It consists of the water

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molecules which have had sufficient time, and strong enough attraction for the cation to orient themselves differently from those of the bulk water structure [3]. The influence of the metal ion still affects a certain extended environment in the aqueous phase, which is more difficult to define. The molecules that are outside the primary shell but whose behaviour and arrangement are still under the influence of the metal ion are called as secondary hydration shell or outer hydration shell. Lastly, the third group of water molecules which are unaffected forms the bulk aqueous phase [4].

Even close to a century of active research and interest in the area of the characterization of ion solvation properties in aqueous phases, a precise nature of hydration of a salt in an aqueous media is not fully understood. The characterization methods used in determining hydration number, reported in early literatures, are compressibility, dielectric constant, entropy, partial molar volume and Stokes volume [3]. Recently neutron diffraction, X-ray diffraction and *ab initio* molecular dynamics are also engaged extensively [5]. However, these methods do not give common values for hydration number of a cation and the values reported varies greatly [5]. Now these studies take on even greater significance as current biological research targets a molecular understanding of ion solvation in biological environments, where interest lies in the mechanisms controlling ion binding to molecules and selective ion permeation through narrow channel proteins [6].

After the discovery of electronically conducting polymers in the 1970s, continuous experimental and theoretical investigations of this group of polymer materials have explored a realm of new possibilities for both basic research and applications [7]. In addition, this novel group of polymer materials may be used as a unique chemical environment to examine fundamental physical and chemical phenomena, which are not yet precisely uncovered due to experimental constraints: i.e. in a simple and direct method, the hydration number of ions may be systematically determined using electrochemical insertion of ions in a conducting polymer. This version of primary hydration number could be called membrane hydration number.

Recently, our group has successfully demonstrated and reported that the primary hydration numbers of alkali metal cations can directly and accurately be determined using the unique physico-chemical environment of polypyrrole (PPy) doped with the large, immobile dodecylbenzene sulfonate (DBS) anions operating in aqueous electrolytes [8]. The first electrochemical cathodic reduction of a freshly prepared PPy(DBS) film, which is in an oxidative form, operating in aqueous phase containing hydrated cations, has been used. The present work aims to further extend the studies for determining reliable values for membrane hydration

numbers of alkali earth and alkali rare earth metal cations using the same method adopted in [8] and to explore any possible common trends among the membrane hydration number values obtained for the cations. The membrane hydration numbers of alkali earth and alkali rare earth metal cations in respective chloride aqueous electrolytes having various concentrations ranging from 0.02 to 1 M determined using PPy(DBS) conducting polymer are reported in this paper.

## Experimental

PPy(DBS) films were electropolymerized on AT-cut quartz crystal electrodes with a constant current density of 1 mA/cm<sup>2</sup> as described elsewhere [9]. The chosen current density produces very sharply defined reduction peaks—equal to those obtained using smaller anions at low (<0.1 mA/cm<sup>2</sup>) current densities. The polymerization electrolyte consisted of 0.05 M sodium dodecyl benzene sulfonate (SDBS, Fluka Technical). Analysis showed no significant amounts of sulphate) and 0.05 M pyrrole monomer in pure water. The current and time was chosen to form a film of ~400 nm thickness, calculated from assuming that a charge passed during synthesis of 160 mC/cm<sup>2</sup> yields a 1- $\mu$ m coating [10]. The precise thickness of the film (which changes on ion insertion), is not important to the present experiments. Simultaneous cyclic voltammetry (CV) and differential mass detection was performed on the deposited PPy(DBS) film. An electrochemical quartz crystal microbalance (EQCM) using an ICM 10 MHz crystal with a 0.20-cm<sup>2</sup> gold electrodes controlled by a Hewlett-Packard E4916A crystal analyzer in combination with a potentiostat (Autolab PGSTAT 30) were used to measure the change of mass during insertion of solvated ions. The cycling experiments with simultaneous CV and EQCM measurements were done in aqueous MgCl<sub>2</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub>, SrCl<sub>2</sub>, YCl<sub>3</sub> and LaCl<sub>3</sub> electrolytes having various concentrations ranging from 0.02 to 1 M. For each experiment, a freshly prepared PPy(DBS) film of 400 nm thickness polymerized under the same experimental conditions was used. For all cycling, a constant scan rate of 2 mV/s was used as optimized in [8]. At this rate, or lower, the ions have time to penetrate the full thickness of the film. Faster scan rates would result in only a fraction of the film being active.

## Results and discussion

Simultaneous cyclic voltammograms (solid lines) and the corresponding frequency changes (dashed lines) from EQCM measurements obtained for PPy/DBS films cycled

in 0.1 M  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{LaCl}_3$ , and  $\text{YCl}_3$  are shown in Fig. 1. The pristine film was first cathodically reduced from 0.0 to  $-0.9$  V ( $\sim$ ) and subsequently oxidized to between  $+0.1$  and  $+0.5$  V to complete the first complete reduction + most of the oxidation (pointed by long arrow direction in Fig. 1). As seen in the figures, the main feature

of the cyclic voltammogram in each experiment is a sharp reduction peak during cathodic reduction of the film, centred at  $-0.6$  V versus Ag/AgCl in 3 M KCl. Since the PPy film is synthesised by oxidation, there are no cations inside the pristine film. The only ions are the large, immobile  $\text{DBS}^-$  ions countering the positive charge on

**Fig. 1** First full cycle of a 400-nm polymer in **a** 0.10 M  $\text{MgCl}_2$ ; **b**  $\text{CaCl}_2$ ; **c**  $\text{SrCl}_2$ ; **d**  $\text{BaCl}_2$ ; and **e**  $\text{LaCl}_3$ ; **f**  $\text{YCl}_3$ . *Full curve*—Current during redox cycling (negative values, Reduction). *Dashed curve*—EQCM frequency relative to 10 MHz. The sweep starts at  $+0.0$  V at 2 mV/s. Note the sharpness of the reduction peak centred at about  $-0.6$  V for most cations. The current and the frequency scales are the same for all figures to enable direct comparison

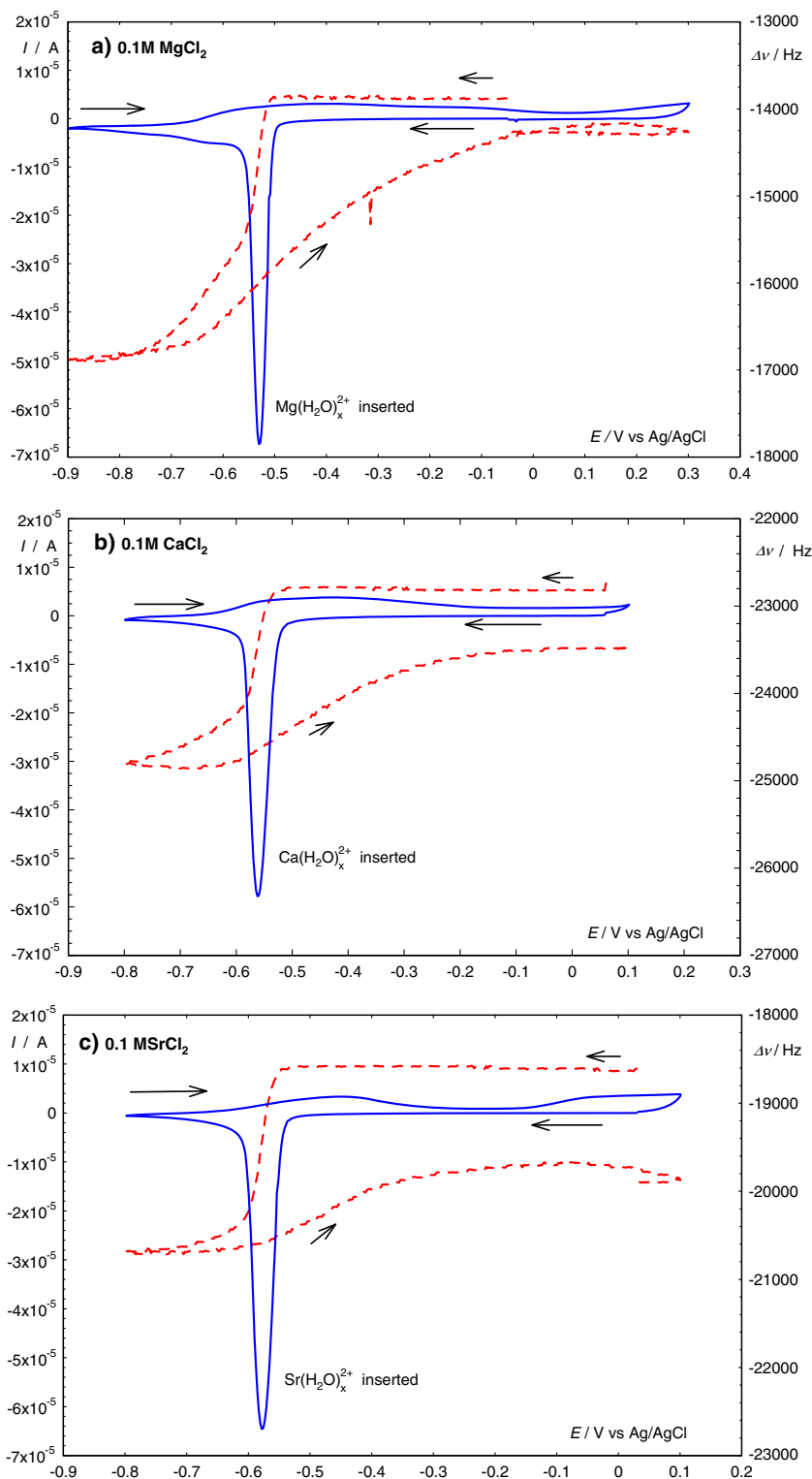
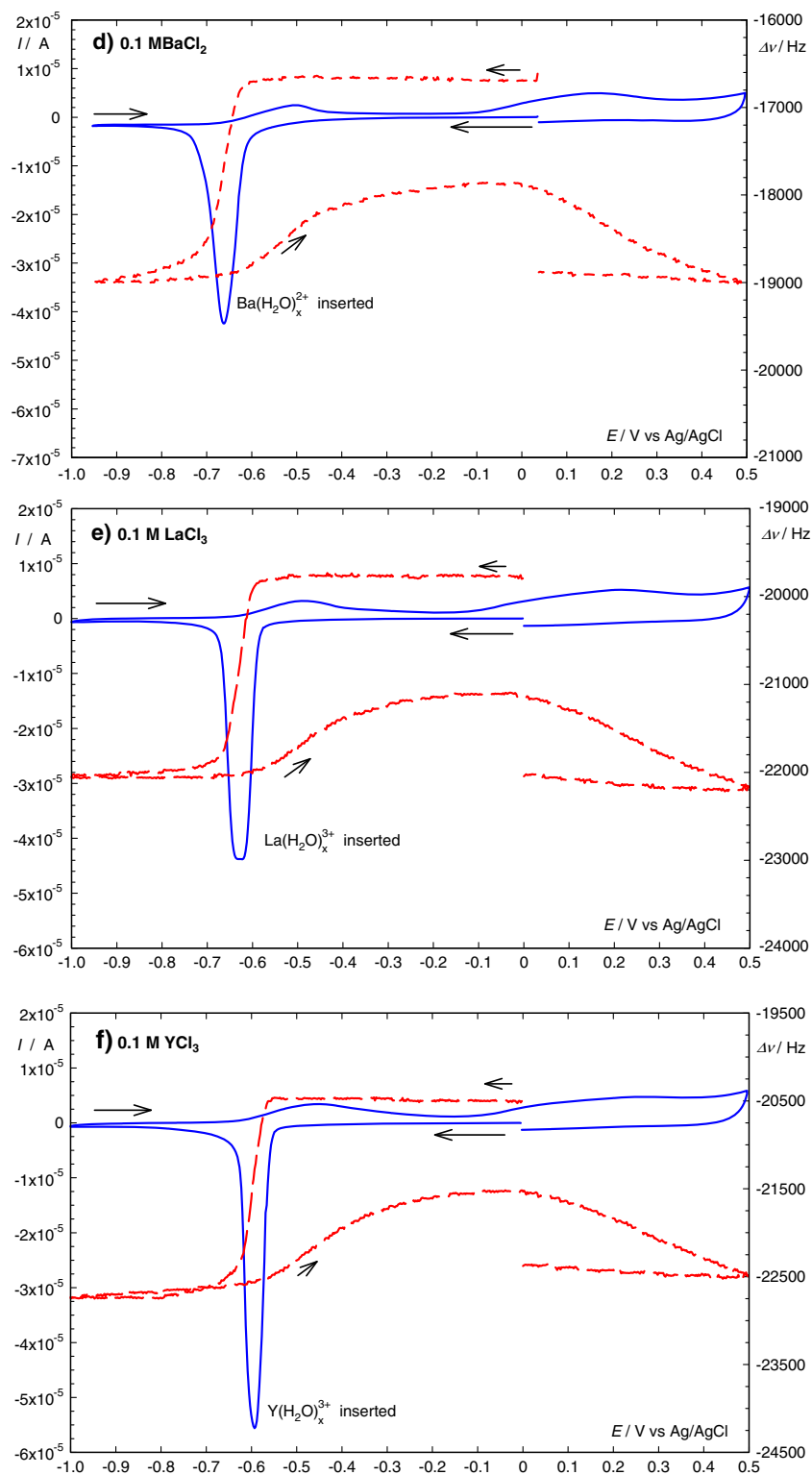


Fig. 1 (continued)



the polymer backbone. Moreover, these  $\text{DBS}^-$  anions are permanently fixed inside the film and are not involved in any subsequent redox mechanism because of the large size and strong entanglement between polymer chains. Hence, the first reduction therefore consists solely of the insertion

of cation  $\text{M}^+$  (plus possible neutral water molecules) present in the cycling electrolyte into the polymer. More importantly, there are no complications arising from simultaneous anion expulsion possible in the first reduction of the film [11, 12]. In this context, the analysis of the first

**Table 1** Selected values of reported hydration numbers of metal cations

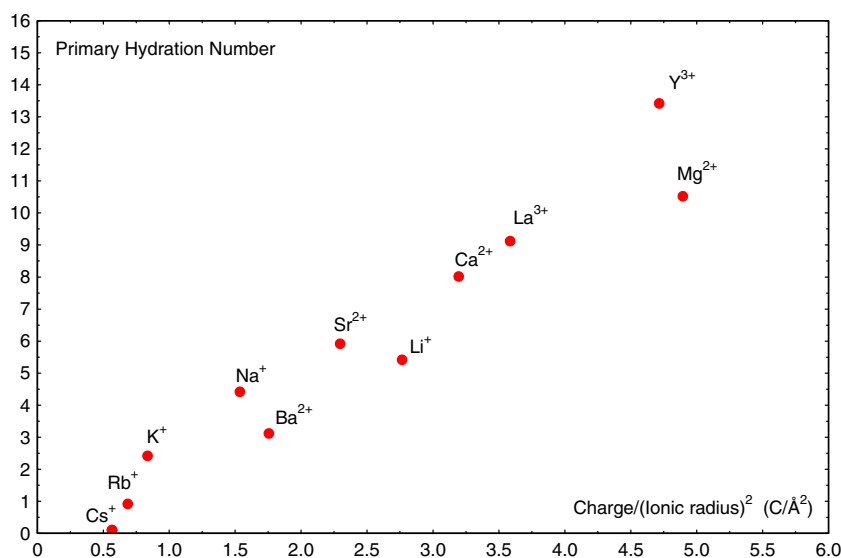
M <sup>+</sup>	Method/Comment						
	Conducting polymer insertion	Several in summary review	Ab initio overview	X-ray diffraction	Neutron diffraction	Pulse NMR	Column size exclusion
Li <sup>+</sup>	5.3–5.5*	5±1	4	4	6	–	0.64
Na <sup>+</sup>	4.3–4.5*	5±1	4	4	8	6	0.22
K <sup>+</sup>	2.0–2.2*	4±2	4	6	8	8	≅0
Rb <sup>+</sup>	0.8–0.9*	3±1	–	–	–	–	–
Cs <sup>+</sup>	0*	–	–	–	–	–	–
Mg <sup>2+</sup>	10.4–10.6	13–16	–	–	–	6	–
Ca <sup>2+</sup>	7.9–8.1	7.5–10.5	–	–	–	6	–
Sr <sup>2+</sup>	5.7–6.1	–	–	–	–	–	–
Ba <sup>2+</sup>	3.0–3.1	–	–	–	–	–	–
La <sup>3+</sup>	9.0–9.1	–	9	–	–	–	–
Y <sup>3+</sup>	13.6–13.8	–	–	–	–	–	–
Ref #	This work (*reported in 8)	[1]	[5]	[17]	[18, 19]	[4]	[20]

reduction process becomes simple and the amount of M<sup>+</sup> ions inserted is determined by being directly proportional to the area of the reduction peak. The charge of the M<sup>+</sup> moved in (the number of moles of M<sup>+</sup>) can be found from the area covered by the cathodic peak with reference to the zero current as the base line.

The frequency measurements during the cathodic reduction of the films give information about all moving species, both M<sup>+</sup> and water molecules, into the film. On closer inspection of Fig. 1, the frequency curve during reduction can be clearly divided into three segments: No redox reaction—no frequency change; sharp reduction peak—a very steep frequency decrease; no significant redox reaction—but a large, continuous, but less steep frequency decrease. At end of

the peak, there is a distinct shift in slope of the frequency curve. Furthermore, the steepest part of the curve corresponds closely to the maximum of the reduction peak. The beginning and the end of the steep part also coincide closely with the beginning and end of the reduction peak. This leads to the identification of the mass change of the steep part with the insertion of the M<sup>+</sup> ion together with tightly bound H<sub>2</sub>O molecules, i.e. those of the inner hydration shell that are associated directly with the cation only. From the steep part of the frequency measurements in complement with cyclic voltammetry measurements, the number of moles of tightly bound H<sub>2</sub>O with M<sup>+</sup> can be estimated. Hence, the primary hydration number can now be determined as the number of moles of tightly bound H<sub>2</sub>O, divided by the number of moles

**Fig. 2** Variation of primary hydration numbers of metal ions as a function of the charge divided by the square of the crystal radius



of  $M^+$  ions inserted, determined by the area of the reduction peak.

To minimize the errors and eliminate uncertainties, we have now further refined the method of finding the inserted amount of cations from the charge resulting in more precise values. Only the first part of the reduction is used—this prevents interference from the osmotic inserted water that dominates the mass increase at lower potentials. A second method involves graphical integration by visual inspection of the full first half of the reduction. The methods yield only slightly different and robust results. The hydration numbers obtained are not simply a statistical average over the time of insertion, since earlier work has shown that the ratio between the mass and the charge inserted is constant during the full first half of the reduction, and is therefore a well-defined characteristic of the insertion process [13].

The membrane hydration numbers obtained for alkali, alkali earth and two rare earth metal cations by this novel method in this work and in our earlier work are summarised in Table 1 together with selected primary hydration number values obtained by other methods [8].

It must be emphasised that the data in the table are not exhaustive, but are chosen to show the large span of values—both with respect to absolute hydration numbers, and with respect to trends in the metal ions. To a certain degree, the differences reflect that the methods probe different aspects of the hydration phenomenon. In addition, methods that use a static arrangement of ions will typically yield integer values (~coordination numbers), whereas our method yields dynamic averages that may have non-integer values. The most important result is the clear distinction between the metal cations. The method seems to measure real and significant properties of the solvated ions. The membrane hydration numbers obtained in electrolyte concentrations of 0.02 and 1 M for the cations yields similar values although 0.1 M yields the best accuracy. Part of the reasons for the discrepancies may be the different time constants of the various methods—the present method is rather slow (tens of seconds).

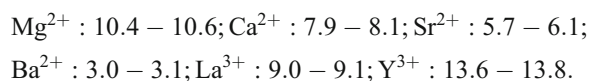
In order to study a possible trend, the variations of the primary hydration numbers of alkali and alkali earth metal ions as a function of the nominal charge density of the ions, charge/(crystal radius)<sup>2</sup> where the radius corresponds to the Shannon radius [14, 15], were plotted and the variations are shown in Fig. 2.

As seen in the figure, the variations of hydration number vs. nominal charge density for the two cation series plus  $Y^{3+}$  and  $La^{3+}$  follow approximately the same mathematical relation. It can be concluded that the surface charge density of a cation plays an important role in the formation of the hydration shells in an electrolyte and in

determining the primary hydration number of a cation. The model using the surface charge density may well be the best simple model to predict the primary hydration shell—improvements would probably require much more sophisticated, quantum chemical calculations. This finding is in accord with old ideas of solvation numbers, but not with many more recent theoretical and experimental results. It should be emphasised that the method is in no way biased for or against any model of the solvation process. The EQCM method used in this work was pioneered in the study of sorption of ions into polymers in 1990 [16]

## Conclusion

The hydration numbers of metal cations in aqueous electrolytes have been determined using the novel physico-chemical environment of polypyrrole. The primary (membrane) hydration numbers obtained for alkali earth and alkali rare earth metal cations in respective chloride aqueous electrolytes having low to moderate concentrations (0.02–1 M) are:



The values of the primary hydration numbers of these metal ions are found to remain constant in the above aqueous electrolytes having concentrations up to 1 M. Since the results for the diverse set of cations are robust with respect to concentration, we believe that the values are representative of the hydration in the bulk water phase.

For all cations, the primary hydration numbers show a simple dependence on the total charge per surface area of each cation, which is a measure of the surface charge density. The model using the surface charge density may well be the best simple model to predict the primary hydration number of a metal ion.

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