

A Raman Study of Alcoholic Lithium Perchlorate Solutions in the Glassy State

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

Raman spectra of alcoholic lithium perchlorate solutions (alcohol = methanol and ethanol) were measured as a function of LiClO_4 concentration. The Raman band due to nearly free hydrogen bonds shows peculiar concentration dependences: (1) its frequency shifts with LiClO_4 concentration in contrast to alcoholic LiX solutions ($\text{X} = \text{Cl}$ and Br), in which the Raman band due to solvated halide ions shows little frequency change with LiX concentration, and (2) the half band width shows anomalous changes with LiX concentration.

Non-ionized LiClO_4 species in alcohol coupled with the changes of solution structure are the major cause for this peculiar behavior.

Key words: Raman spectra; Alcohol solution; Glassy state; Lithium perchlorate; OH stretching spectrum.

1. Introduction

When a large anion is dissolved in water, hydrogen bonds between water molecules are destroyed and weak new hydrogen bonds are formed between the dissolved anion and its surrounding water molecules [1, 2]. Perchlorate ion is a typical large structure-breaking ion, and the Raman OH stretching spectra for aqueous solutions of perchlorates have been discussed in detail from various points of view [1–5]. A sharp peak at around 3570 cm^{-1} in a Raman OH stretching spectrum is now attributed to the OH stretching modes of water molecules weakly hydrogen bonded to perchlorate ions. The hydrogen bonds between water molecules and perchlorate ions are so weak that they are often called as nearly free hydrogen bonds [4, 5]. A similar Raman band is observed for methanolic perchlorate solutions at ambient temperatures.

In view of the fact that the Raman spectrum for a glassy solution is more suitable for characterization of the solution than that for the liquid solution at room temperature [5], we measured Raman spectra of methanol and ethanol solutions of LiClO_4 in the glassy state as a function of the salt concentration and discussed the effect of perchlorate ions on the OH stretching Raman spectra of alcohols.

2. Experimental

Alcoholic lithium perchlorate solutions were prepared by dissolving anhydrous lithium perchlorate in absolute alcohol (methanol and ethanol: purity $>99.5\text{ wt}\%$). Here the salt concentration of the solutions is expressed by Y (= moles of solvent/moles of salt). Raman spectra were measured by a JASCO NR-1100 spectrometer using $\sim 300\text{ mW}$ of the 514.5 nm line of an NEC argon ion laser as an exciting source. When measuring Raman spectra of glassy samples, a specially designed Dewar vessel was used to maintain a glassy sample at liquid nitrogen temperature. Vitrification of a sample solution was achieved by immersing the sample solution in a Raman cell into liquid nitrogen. The overall cooling rate was about $4 \times 10^2\text{ K/min}$.

3. Results and Discussion

Figure 1 shows the Raman OH stretching spectra of methanolic LiClO_4 solutions in liquid and glassy states.

As the concentration of perchlorate ions increases, the high frequency region at around 3530 cm^{-1} grows to become higher than the lower frequency region centered at 3330 cm^{-1} . This high frequency region is clearly due to the OH stretching vibrations of methanol molecules weakly hydrogen bonded to ClO_4^- ions.

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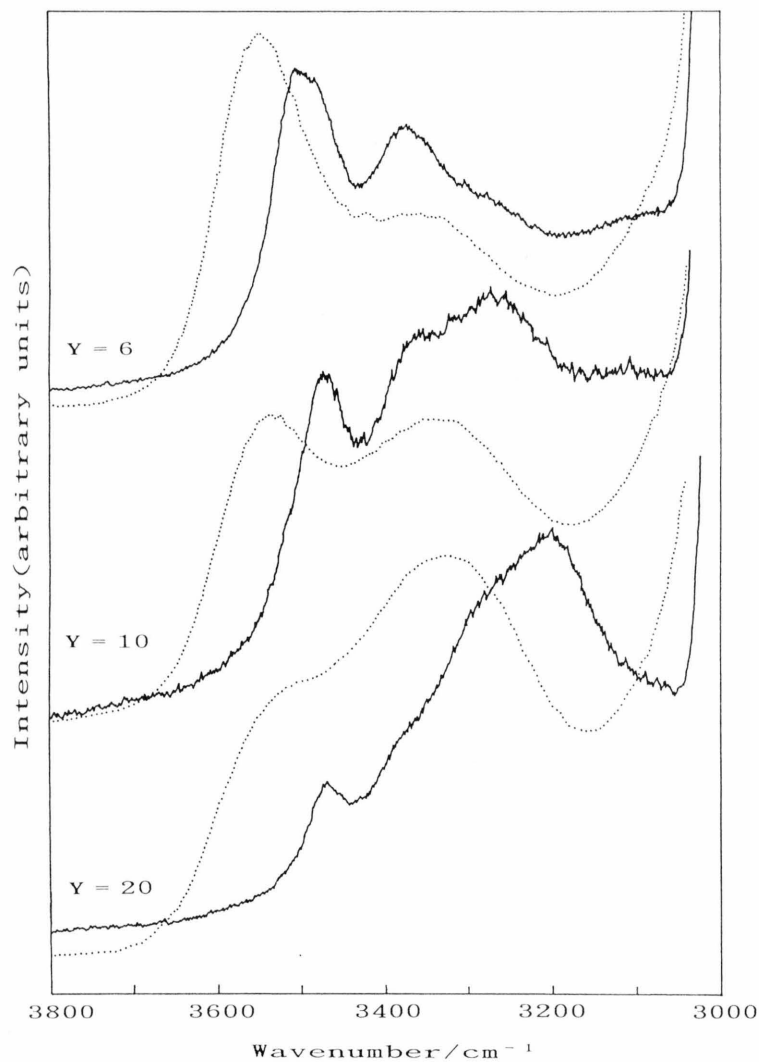


Fig. 1. Raman spectral changes of methanolic lithium perchlorate solutions with molar ratio Y . Dotted curve: liquid state at room temperature. Solid curve: glassy state at liquid nitrogen temperature.

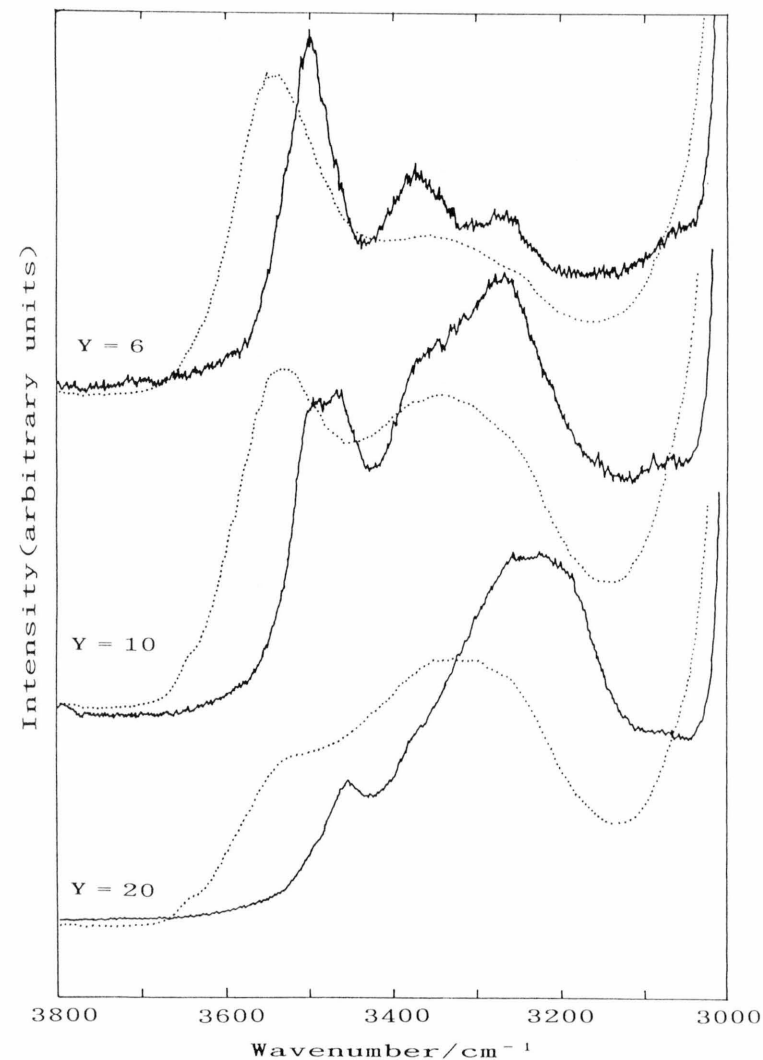


Fig. 2. Raman spectral changes of ethanolic lithium perchlorate solutions with molar ratio Y . Dotted curve: liquid state at room temperature. Solid curve: glassy state at liquid nitrogen temperature.

An interesting aspect of the Raman spectra for the solutions at room temperature is the gradual increase in the peak frequency of the high frequency region with increase in perchlorate concentration. The highest peak at about 3325 cm^{-1} in the Raman spectrum for the $Y = 20$ solution moves to at about 3339 cm^{-1} for the $Y = 10$ solution and its intensity decreases with the decrease of the Y value, indicating that the intrinsic liquid structure of methanol is gradually disrupted and instead the high frequency region grows. This is a common feature of a Raman OH stretching spectrum for every electrolyte solution at ambient temperature [6] and is a clear indication that the hydrogen bonds between perchlorate ions and methanol molecules become weaker. As perchlorate ion is a strong structure breaker, the strong hydrogen bonds among alcohol molecules are disrupted by dissolved ClO_4^- ions and weak hydrogen bonds are formed between ClO_4^- ions and surrounding alcohol molecules.

Hester and Plane [7] made a Raman study to see the effects of electrolytes on the Raman spectrum of methanol and found that the OH frequency is raised in the order $\text{H}_2\text{O} < \text{F}^- < \text{Cl}^- < \text{SO}_4^{2-} < \text{NO}_3^- < \text{ClO}_4^-$, consistent with the increasing order of the structure breaking power of the ions.

It is now well established that vitrification enhances the characteristic features of the structure of a solution [8].

A remarkable point about the Raman spectra for the glassy methanolic LiClO_4 solutions is that the gradual increase of the wavenumber of the high frequency peak with increase in perchlorate ions.

The peak at 3466 cm^{-1} in the $Y = 20$ solution moves to 3473 cm^{-1} in the $Y = 10$ solution and to around 3495 cm^{-1} in the $Y = 6$ solution.

This is a clear contrast to the corresponding peak frequency for a glassy aqueous perchlorate solution in which the peak frequency changes little with salt concentration [5]. A similar contrast is observed for the peak frequency of the Raman band due to solvated halide ions $[\text{X}(\text{HOMe})_n]^-$ in glassy methanolic LiX solution (MeOH: methanol): the peak frequency (at 3385 cm^{-1}) for a glassy methanolic LiCl solution remains unchanged from $Y = 40$ to $Y = 6$ [6].

It is important to point out that a similar wavenumber change is observed for the $\text{LiClO}_4 \cdot Y(\text{C}_2\text{H}_5\text{OH})$ solutions (Figure 2).

Another peculiar feature of the Raman spectra of the glassy ethanolic LiClO_4 solutions is that the peak

becomes broad at $Y = 10$ but gets back to a sharp band at $Y = 6$. As the peak splits at $Y = 10$, it is clear that there are at least two components responsible for this behavior.

When the concentration of LiClO_4 is low, most of the perchlorate molecules are considered to ionize in alcohol. Therefore, the peak at $\sim 3452\text{ cm}^{-1}$ ($\sim 3466\text{ cm}^{-1}$ for the glassy $\text{LiClO}_4 \cdot 20\text{ MeOH}$ solution) in the glassy $\text{LiClO}_4 \cdot 20\text{ EtOH}$ solution (EtOH: ethanol) is mainly attributed to the OH stretching vibrations of alcohol molecules weakly hydrogen-bonded to ClO_4^- ions.

As the dielectric constant of alcohol is lower than that of water, it is conceivable that dissolved LiClO_4 exists in nonionized form such as contact ion pairs in alcohol solutions of high salt concentrations, in particular at low temperatures.

Therefore, the peak at $\sim 3495\text{ cm}^{-1}$ in the $\text{LiClO}_4 \cdot 6\text{ EtOH}$ solution is probably mainly due to the OH stretching vibrations of the alcohol molecules surrounding the non-ionized LiClO_4 molecules (contact ion pairs).

If inert molecules such as CCl_4 and benzene are dissolved in an alcohol, the hydrogen bonds between alcohol molecules around the dissolved inert molecules are broken or become very weak and a Raman band, due to the OH groups having no hydrogen bonds with other alcohol molecules, comes out in the wavenumber region above 3600 cm^{-1} . This band is usually called a free-hydrogen Raman band [10, 11]. The wavenumber of the band is 3645 cm^{-1} for the $\text{MeOH}-\text{CCl}_4$ solution and 3630 cm^{-1} for the $\text{EtOH}-\text{CCl}_4$ solution.

Thus it is clear that the interactions between a non-ionized LiClO_4 and its surrounding alcohol molecules are "fairly strong" in the sense that the peak frequency ($\sim 3495\text{ cm}^{-1}$ for both methanol and ethanol solutions in the glassy state) is by more than 100 cm^{-1} lower than the one for the free hydrogen bonds.

For aqueous solutions it is reported that the decrease of the OH stretching frequency by 50 cm^{-1} roughly corresponds to the increase of the hydrogen bond strength by 1 kcal/mol [12, 13].

If we apply this empirical rule to alcoholic solutions, we can estimate the average hydrogen bond strength between a non-ionized LiClO_4 molecule and its surrounding alcohol molecules to be around 2 kcal/mol .

One of the notable features associated with vitrification of the alcoholic LiClO_4 solutions is that the struc-

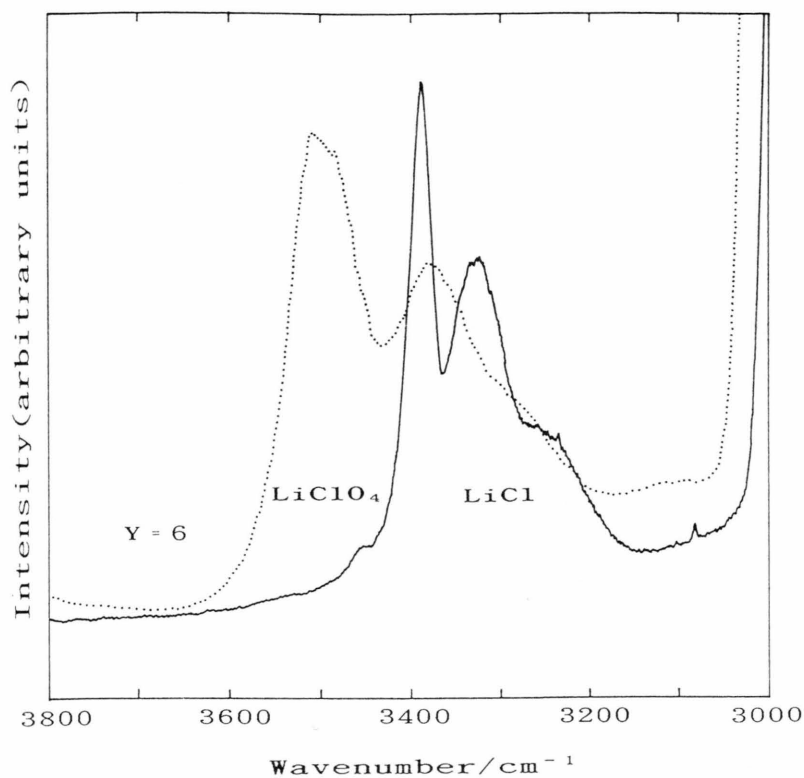
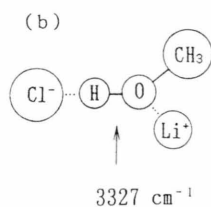
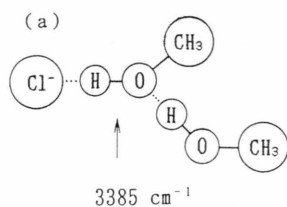


Fig. 3. Raman OH stretching spectra for methanolic LiCl and LiClO_4 solutions ($Y = 6$) in the glassy state. Dotted curve: glassy $\text{LiClO}_4 \cdot 6 \text{ MeOH}$ solution. Solid curve: glassy $\text{LiCl} \cdot 6 \text{ MeOH}$ solution.

$\text{LiCl} \cdot 6 \text{ MeOH}$ solution



$\text{LiClO}_4 \cdot 6 \text{ MeOH}$ solution

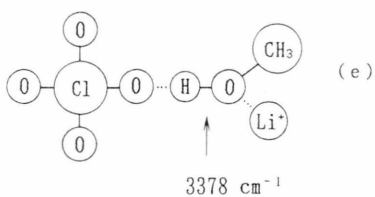
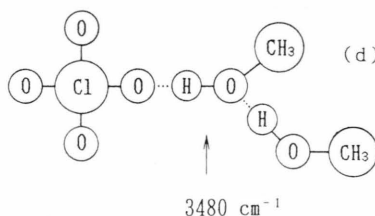
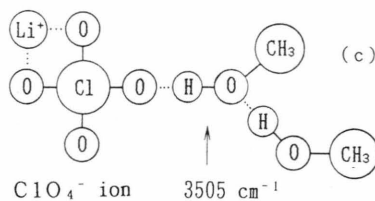


Fig. 4. Configurational models for the anion solvations in glassy $\text{LiClO}_4 \cdot 6 \text{ MeOH}$ and $\text{LiCl} \cdot 6 \text{ MeOH}$ solutions.

tural changes on going from the liquid state at room temperature to the glassy state becomes smaller with increase in salt concentration.

In the $\text{LiClO}_4 \cdot 20 \text{ MeOH}$ solution the peak at $\sim 3330 \text{ cm}^{-1}$ moves to $\sim 3200 \text{ cm}^{-1}$ on vitrification while in the $\text{LiClO}_4 \cdot 6 \text{ MeOH}$ solution the peak at $\sim 3550 \text{ cm}^{-1}$ shifts to $\sim 3500 \text{ cm}^{-1}$ in the glassy solution. This trend is considered to be associated with the disruption of strong hydrogen bonds. Since most hydrogen bonds are nearly broken or severely weakened by neighboring cations and anions in a highly concentrated perchlorate solution, it is conceivable that they can not restore their original strengths even at low temperatures. In fact, a large spectral change with a large frequency shift is observed for liquid methanol and ethanol on vitrification. In vitrified methanol (ethanol) most hydrogen bonds are strong, as evidenced with a strong sharp Raman peak at $\sim 3200 \text{ cm}^{-1}$ [6].

Here it is important to compare the Raman spectra of glassy LiCl and LiClO_4 solutions. From Fig. 3 it is evident that two spectra are similar in their spectral contours though the peak frequencies are different. Therefore, inference from the peak assignments for the chloride solution is useful for the assignments of the peaks for the perchlorate solution.

In the glassy lithium chloride solution, the sharp peak at 3385 cm^{-1} was assigned to the OH stretching vibration of the methanol molecules weakly hydrogen bonded to chloride ions and also bonded to other methanol molecules with their lone pairs of oxygens (depicted in Figure 4a).

The relatively broad peak at 3327 cm^{-1} is ascribed to the OH stretching vibrations of the methanol molecules in the solvent shared ion pairs (Figure 4b). The clear cationic effect on the peak frequency indicates that there is direct interaction between the cation and the methanol molecule responsible for the Raman peak. The oxygen atom of the methanol molecule is polarized and attracts the electron cloud from the hydrogen atom of the OH group, thereby enhancing the strength of the hydrogen bond between the methanol molecule and its coordinated chloride ion.

Based on these assignments for the chloride solution, the following assignments were made for the lithium perchlorate solution: As already noted, the high frequency component ($\sim 3505 \text{ cm}^{-1}$) of the peak at 3495 cm^{-1} in the $Y = 6$ solution can be attributed to the OH stretching vibrations of the methanol molecules solvating around the contact ion pairs $\text{Li}^+ \text{ClO}_4^-$ (Figure 4c).

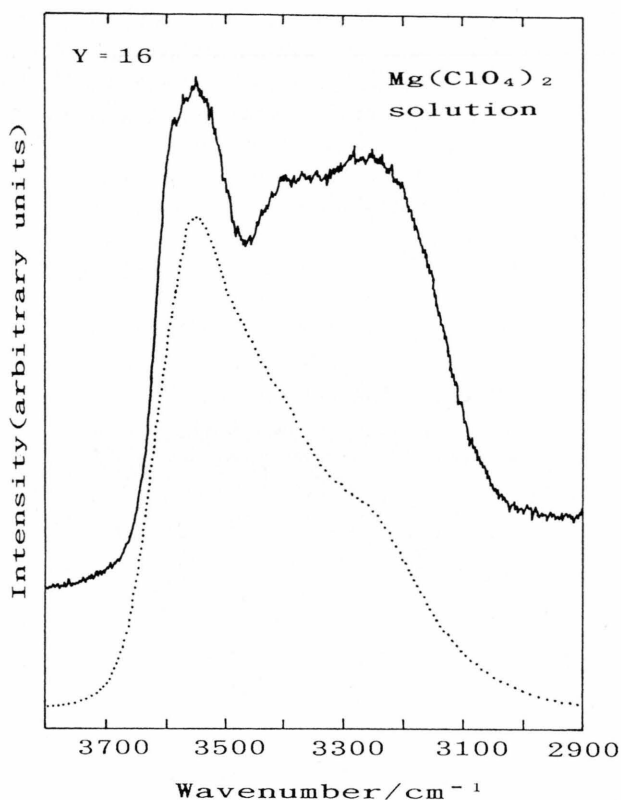


Fig. 5. Raman OH stretching spectra for aqueous $\text{Mg}(\text{ClO}_4)_2$ solution in both liquid and glassy states. Dotted curve: liquid state. Solid curve: glassy state. The Raman data are from [5].

The lower frequency component ($\sim 3480 \text{ cm}^{-1}$) is assigned to the methanol molecules weakly hydrogen-bonded to perchlorate ions and hydrogen bonded to other methanol molecules (Figure 4d).

The lowest frequency peak at 3378 cm^{-1} in the $Y = 6$ solution is ascribed to the methanol molecules in the solvent shared ion pairs in which they are coordinated to both ClO_4^- and Li^+ ions (Figure 4e).

Two interesting aspects emerge from the comparison of the Raman spectra for aqueous $\text{Mg}(\text{ClO}_4)_2$ and methanolic LiClO_4 solutions (Figure 5). The first is that the peak frequency of the OH stretching vibrations of the water molecules weakly hydrogen bonded to perchlorate ions changes little from the liquid state at room temperature to the glassy state, while that of the methanol molecules in the methanolic perchlorate solution shows an appreciable change (the peak at 3531 cm^{-1} moves to 3473 cm^{-1}).

This indicates that the weak hydrogen bond between water and its coordinated perchlorate ion changes little in its strength with temperature while that between methanol and a perchlorate ion becomes stronger with decreasing temperature.

It is considered that the solvation structure of water molecules around a perchlorate ion is rather rigid in contrast to that of alcohol molecules around a perchlorate ion, which changes in its strength with temperature.

From the molar ratio Y of solvent/ ClO_4^- , the aqueous $\text{Mg}(\text{ClO}_4)_2$ solution corresponds approximately to the methanolic LiClO_4 solution of $Y = 8$. The Raman spectrum of the $\text{LiClO}_4 \cdot 6 \text{ MeOH}$ solution at room temperature shows two peaks (one at $\sim 3350 \text{ cm}^{-1}$ and the other at 3547 cm^{-1}), indicating that the intrinsic liquid structure for pure methanol remains to some extent, although mostly disrupted by coexisting solvated Li^+ and ClO_4^- ions.

The other interesting point is that, although the frequency shifts are large, the overall Raman spectral changes are rather small for alcoholic LiClO_4 solutions on vitrification, in contrast to the large spectral changes of the aqueous $\text{Mg}(\text{ClO}_4)_2$ solution ($Y = 16$) associated with glassification.

The significant increase of the Raman intensity in the low wavenumber region ($3100 \sim 3300 \text{ cm}^{-1}$) in the Raman OH stretching spectrum for the glassy aqueous $\text{Mg}(\text{ClO}_4)_2$ solution of $Y = 16$ suggests that the water molecules not existing in the vicinity of perchlorate ion(s) restore strong hydrogen bonds with neighboring water molecules at low temperatures.

From these observations, it may be concluded that, as compared with a corresponding aqueous solution, the structural changes of an alcoholic lithium perchlorate solution are small on vitrification.

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