Optical Fiber Sensor for Determination of Methanol Ratio in Methanol-Doped Ethanol Based on Two Cholesteric Liquid Crystal Droplets Embedded in Chitosan

Yueming Su, Zeqing Lan, Jiaming Wang, Li Zeng, Dong Zhou, Zenghui Peng, Weimin Sun, and Yongjun Liu

***Abstract*—In this paper, an optical fiber sensor based on cholesteric liquid crystal (CLC) is designed to detect the proportion and concentration of methanol and ethanol in alcohol solution. Due to the different polarity of methanol and ethanol molecules, the pitch of CLC will swell in different degrees. Therefore, the reflected light wavelength of CLCs will shift differently when the sensor is put into the mixed solution of two alcohols with different proportions and concentrations. The function of chitosan polymer network is to fix and protect CLC droplets, it also allows small molecules to pass through and interact with CLC. The sensitivities of the two CLCs are 0.296 nm/v% and 0.467 nm/v% to methanol, and 0.764 nm/v% and 1.133 nm/v% to ethanol, respectively. The detection range of the sensor for alcohol solution is 0.5v/v% –30v/v%. The linear relationship between wavelength shift and proportion and total concentration was obtained by least square method, and the related characteristics of the sensor were explored.**

***Index Terms*—Cholesteric liquid crystal, ethanol detection, fiber sensor, hydrogel, methanol detection.**

I. Introduction

METHANOL and ethanol are two kinds of common alcohols, although there is no significant difference in their properties. However, in contrast to the non-toxic nature of ethanol, methanol is highly toxic to human body. Methanol intake and absorption through the skin can cause tissue damage in the human body, from dizziness, vomiting and diarrhea to blindness and even death in severe cases. Methanol may be produced during the fermentation of alcoholic beverages. Since the price of methanol is lower than that of ethanol, some illegal merchants deliberately adulterate alcoholic beverages with methanol, seriously endangering the lives and health of consumers. Therefore, it's of great significance to study the concentration of methanol in ethanol environment.

Liquid crystal (LC) is a soft material that is sensitive to stimuli. The properties of LC will change due to changes in the surrounding environment and the action of substances, and LC also has the advantages of high sensitivity, good repeatability and good biocompatibility, so it is widely used in physical sensing [1]–[4], chemical sensing [5]–[9], and biological [10]–[12] sensing and other sensing fields. The molecules in the cholesteric liquid crystal (CLC) are continuously twisted, and the distance between the two sections corresponding to the molecular twist 2π is the pitch (p) [13]. Due to this special spiral structure, it has a very special optical effect, the circularly polarized light whose spiral direction is consistent with itself is completely reflected when the light wavelength λ is between the band edges of $n_o p$ and $n_e p$. The circularly polarized light with the opposite spiral direction is completely transmitted. This effect is called selective reflection of CLC. The bandwidth $\Delta\lambda$ of the reflection band is expressed as:

$$\Delta\lambda = \Delta n p \tag{1}$$

Where Δn is the optical anisotropy of the liquid crystal: $\Delta n = n_e\text{-}n_o$.

Therefore, the change in the pitch of the CLC caused by the change of the external environment or the action of certain substances will cause the wavelength of the reflected light to shift. In recent years, CLC has shown promising application prospects in the field of sensing due to its periodic structure on the nanometer scale [14]–[16].

Hydrogel is a three-dimensional cross-linked hydrophilic polymer, which can absorb a lot of water and is insoluble in water. It has good biocompatibility, and small molecules can diffuse or exchange in it. A. F. George [17] et al. proposed a method of cross-linking silver ions and chitosan molecules to form films quickly. Compared with the previous complicated and time-consuming operation, this method is simple to operate, and the entire process only takes less than 2s, which provides great convenience for the application of chitosan hydrogel in

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the field of sensing [18]. J. Deng [19]–[20] et al. combined LC and polymer hydrogel, and proposed a sensor that uses agarose to coat the LC, and detects bile acids by changing the orientation of the LC under polarized optical microscope (POM). Recently, some researches have proposed a sensor platform for hydrogel-encapsulated CLC [21], and the combination of polymer network and CLC has become a current research hotspot in the field of sensing.

At present, many methods have been developed to detect the concentration of methanol in ethanol environment, including high performance liquid chromatography (HPLC) [22], multifunctional nanomaterials [23]–[24], Raman spectroscopy [25]–[26], electrochemical methods [27]–[29], etc. However, the current methods have disadvantages such as complicated operation, high cost, and need professionals to operate. Therefore, it is necessary to develop a method with simple structure, good repeatability, convenient operation and accurate measurement. C. K. Chang [30]–[31] et al. proposed a method that uses material properties to increase the difference in properties between methanol and ethanol, so that the two have different effects on the pitch of CLC to enhance sensing capabilities.

This paper proposes a fiber-optic liquid crystal sensor with simple structure and good stability. The chitosan polymer network is used to fix two CLC droplets with different reflected light central wavelengths in the HCT at the end of the optical fiber. Based on the principle that ethanol and methanol can make p of CLCs change differently, the total concentration and proportion of methanol and ethanol in solution can be accurately detected by monitoring the spectral movement, which has a very practical application value. As far as we know, this is the first time that a polymer network embedded with liquid crystal has been integrated at the end of an optical fiber. The method does not require too complicated operations, and has the advantages of fast response, high stability, and compact structure. It provides a new method for measuring the concentration of methanol and ethanol in solution, which has certain significance in the field of liquid crystal sensing.

II. Materials and Methods

Materials: The materials used in this study are: Acetic acid, anhydrous methanol, anhydrous ethanol, chitosan powder and $AgNO_3$. The cholesteryl derivatives used are cholesteryl chloride, cholesterol oleyl carbonate, cholesteryl chloroformate. The first type of CLC (No. 1) is prepared by mixing cholesteryl chloride-11.7wt%, cholesterol oleyl carbonate-66.7wt%, cholesteryl chloroformate-21.6wt%, and the second type of CLC (No. 2) is produced by mixing cholesteryl chloride-19.2wt%, cholesterol oleyl carbonate-57.7wt%, cholesteryl chloroformate-23.1wt%. All materials were purchased from Beijing inno Chemical Technology Co., Ltd. the solution used in the experiment was prepared with deionized water. The chemical structures of cholesteryl derivatives and chitosan are illustrated in Fig. S1.

Mechanism of interaction between alcohols and CLC: Volatile organic compounds such as methanol and ethanol can be absorbed and interact with CLC, which can physically swell the pitch of CLC and cause wavelength shift ($\Delta\lambda_c$) of the central wavelength of reflected light. The mechanism is shown in Fig. 1(a).

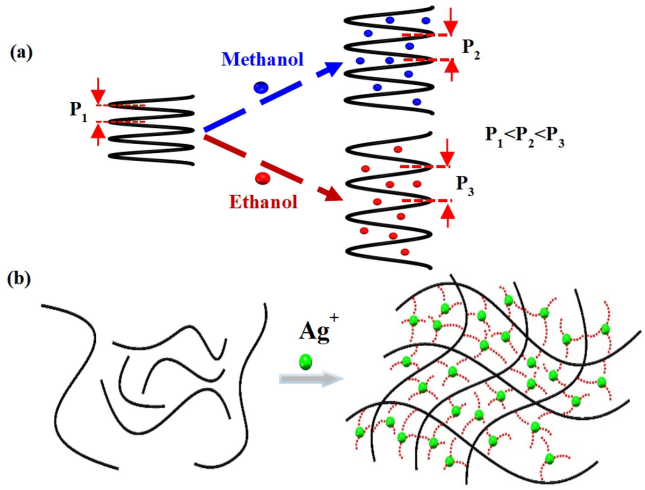

Fig. 1. (a) Schematic diagram of the mechanism of interaction between alcohol molecules and CLC. (b) Schematic diagram of polymer-network hydrogels cross-linked by ultrafast complexation of Ag^+ and chitosan chains.

Preparation of chitosan solution: 0.15g chitosan was dissolved in 10ml 0.5% acetic acid solution. At pH 5.4, 1.5wt% chitosan solution was prepared by stirring with a magnetic stirrer overnight. Fig. 1(b) shows the schematic diagram of polymer-network hydrogels cross-linked by ultrafast complexation of Ag^+ and chitosan chains in water.

Preparation of sensing probe: The fabrication process of the sensor probe is shown in Fig. S2. The hollow capillary tube (HCT) was welded together with the multimode fiber (MMF) by a fiber welding machine. The outer diameter of HCT was 150μm, and the inner diameter was 75μm, the outer diameter of the MMF is 125μm and the inner diameter is 62.5μm. The chitosan solution was injected into HCT through a tapered HCT, which was made by melting and pulling the cone. After that, No.1 CLC and No.2 CLC were injected into the HCT through the tapered HCT, and during the experimental operation, two CLC droplets were placed at the positions corresponding to the optical fiber core. Finally, a few $AgNO_3$ solution was extracted with a capillary cone and slowly injected into the hollow capillary port. After 5s, the tapered HCT was taken out and the chitosan solution in HCT was completely cured.

Fig. 2(a) shows the device diagram of the experiment. The white light emitted by the halogen lamp is coupled to the input port of the MMF coupler and transmitted to the fiber probe part. The reflected light is then received by the spectrometer and fed back to the computer. Fig. 2(b) shows the schematic diagram of the sensing probe. Fig. 2(c) shows the microscope image and POM image of the probe. CLC droplets are immobilized and protected by a chitosan polymer network in HCT. The sensing probe is placed in the alcohol solution to be measured, when the alcohol concentration or the ratio of methanol to ethanol in the solution is changed, the pitch of the CLCs changes, and the wavelength of the reflected light changes accordingly. We

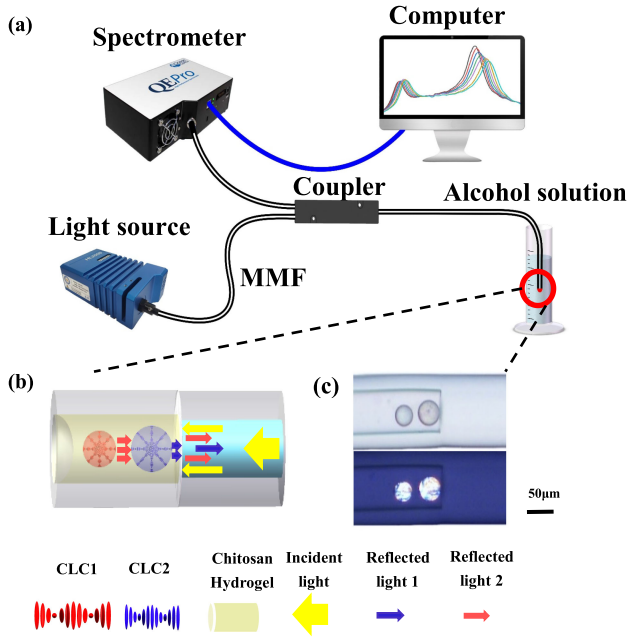

Fig. 2. (a) Schematic diagram of the experimental device. (b) The schematic diagram of the fiber-optic probe. (c) Microscope image and POM image of the probe.

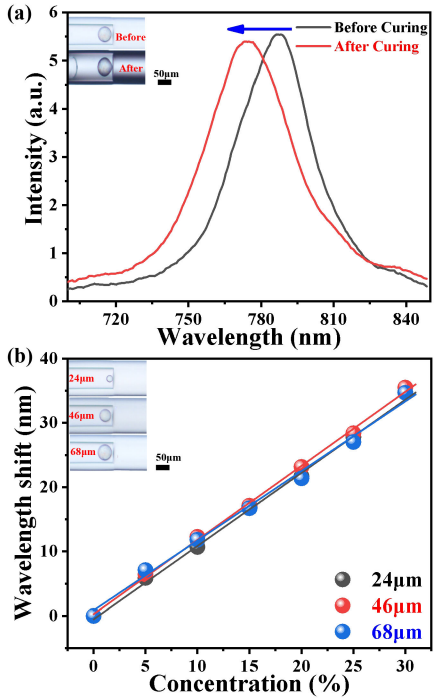

Fig. 3. Influence of experimental operation on sensor characteristics. (a) Influence of curing process on spectrum. (b) Influence of CLC droplet size on sensitivity.

can characterize the proportion and concentration of alcohol in the solution by the change of the received spectrum. In order to reduce the influence of temperature on the experimental results, all the solutions in the experiment were prepared in advance and kept at the same room temperature for more than 6 hours to ensure that the solution temperature was basically the same.

III. Results and Discussion

Effect of chitosan solution curing on CLC: We investigated the effects of chitosan solution before and after curing on CLC, and the results were shown in Fig. 3. Fig. 3(a) shows the spectral shift of the CLC before and after curing. The inset in Fig. 3(a) shows the microscopic images of the probe, the top one is the image before curing, and the bottom one is after curing. The inner arc of the HCT in inset indicates that the chitosan solution forms a polymer network by cross-linking with Ag^{+}. By comparing the images before and after curing, it can be seen that the CLC microspheres inside the chitosan solution are exerted a force during the curing process, resulting in the shrinkage of the CLC microspheres and the decrease of the p of the CLC. The blue shift of the CLC spectrum in Fig. 3(a) also verified our conjecture.

Influence of CLC droplet size on sensitivity: In order to explore the influence of CLC droplet size on alcohol response sensitivity, we used three different sizes of CLC droplet to conduct a comparative experiment. The diameters of CLC droplets were 24μm, 46μm and 68μm. The comparative experiments were carried out in the same environment to exclude the influence of temperature and other environmental factors on the experimental results. The spectral changes of CLC droplets of three different sizes in ethanol environment are shown in Fig. S3. Fig. 3(b) shows the fitting results after repeated measurements. Therefore, we believe that in the range of HCT with an inner diameter of 75μm, the size of CLC microspheres has little effect on the response sensitivity.

Detection range of alcohol solution by sensor: In order to determine the detection range of the sensor for alcohol solution, we use No.2 CLC to measure methanol and ethanol solution separately, and the results are shown in Fig. 4. Firstly, the detection limit for alcohol solutions is explored. Fig. 4(a) and 4(b) correspond to the response curves of NO.2 CLC in low-concentration methanol and ethanol environments, respectively. The inset is a partial enlarged image of the peak part. The dotted line in Fig. 4(a) is the initial spectrum of the light source. By monitoring the spectral changes, we can conclude that the detection limit of the sensor for methanol and ethanol solutions is 0.5v/v% and 0.3v/v%, respectively.

Fig. 4(c) and 4(d) correspond to the response curves of NO.2 CLC in high-concentration methanol and ethanol environments, respectively. Figure S4 shows the fitting curve of wavelength shift and alcohol concentration. It can be seen from Fig. 4(d) that the $\Delta\lambda_c$ of CLC does not increase linearly with the increase of ethanol concentration, but decreases gradually with the increase of ethanol concentration, and the spectral line becomes irregular. This is because the combination of alcohol molecules and CLC molecules will destroy the molecular order of CLC. Therefore, with the increase of ethanol molecules in the solution, more ethanol molecules are needed to change the pitch of CLC. When the solubility of ethanol reached 60%, the response of CLC molecules to ethanol molecules almost reached saturation.

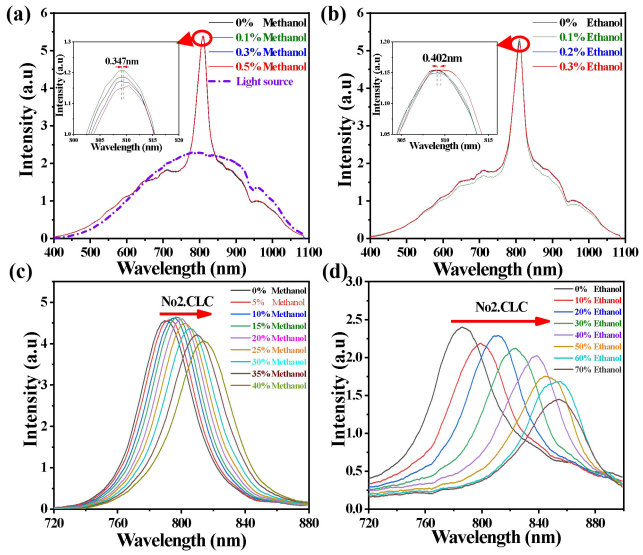

Fig. 4. Spectral changes of No.2 CLC in a low (a) methanol and (b) ethanol concentration environment. Response curve at high (c) methanol and (d) ethanol concentration. The illustration is an enlarged image of the crest part.

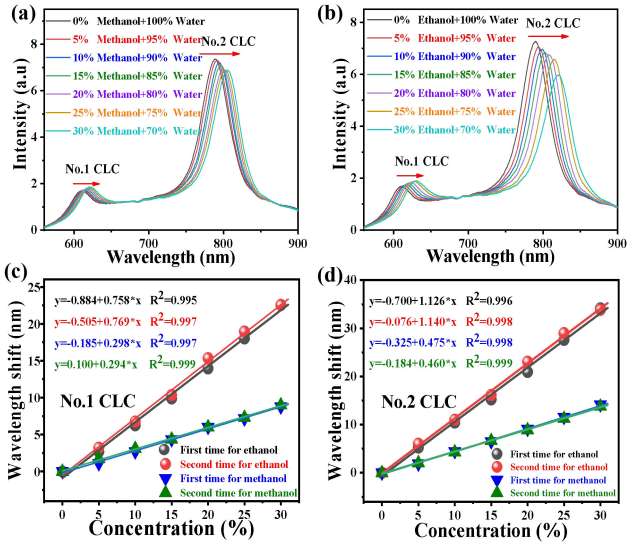

Fig.5. Spectral changes in (a) methanol and (b) ethanol measurement. Sensitivity of (c) No.1 CLC and (d) No.2 CLC to changes in methanol and ethanol concentrations.

Then continue to increase the concentration of ethanol, and λ_c hardly changes. When the concentration of ethanol reaches 80%, the reflection spectrum disappears immediately. Put the probe back into the deionized water. Although λ_c returns to the initial position, the spectrum becomes less sharp than before, and the reflected light intensity also decreases. Therefore, we choose the linear response area of the ethanol and methanol solution as the sensing range. The detection range of the sensor for alcohol solution is 0.5v/v% - 30v/v%.

Fig. 5(a) and 5(b) show the spectral shift images at different methanol and ethanol concentrations, respectively. It can be seen from the Fig. 5 that with the increase of alcohol concentration,

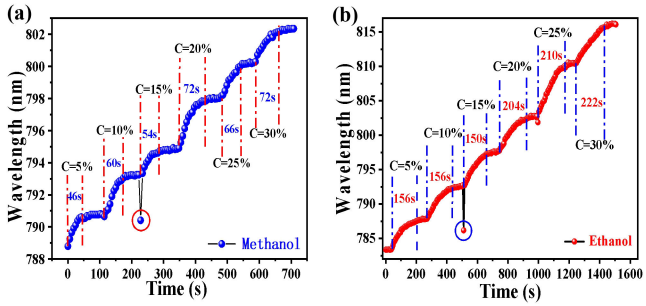

Fig. 6. The response time of No.2 CLC: (a) Methanol and (b) Ethanol.

the λ_c of CLCs has a shift to the long wave direction. The reason is that the alcohol molecules diffuse to the surface of the CLCs droplets through the chitosan film, and interact with the CLCs molecules to increase the pitch of the CLCs and make λ_c redshift. We perform reciprocating measurements on methanol and ethanol and then perform fitting, as shown in Fig. 5(c) and 5(d). The sensitivity of No.1 CLC to methanol and ethanol is 0.296 nm/v% and 0.764 nm/v%, respectively. The sensitivity of No.2 CLC to methanol and ethanol is 0.467 nm/v% and 1.133 nm/v%. The reciprocating measurement deviation of No.1 CLC is 0.68% and 0.78%, the reciprocating measurement deviation of No.2 CLC is 1.50% and 0.62%. It can also be seen that the sensitivity of CLCs to changes in methanol concentration is lower than that of ethanol. This is due to the fact that the polarity of ethanol molecules is greater than that of methanol molecules. Moreover, the sensitivity of No.2 CLC is greater than that of No.1 CLC, which implies that CLC with larger λ_c is more sensitive to alcohols than CLC with smaller λ_c.

Study on the response time of sensors to alcohol: Taking 95% of the equilibrium wavelength as the standard, the response time of No.2 CLC to methanol and ethanol is shown in Fig. 6. It can be seen from Fig. 6(a) and 6(b) that with the increase of methanol and ethanol concentration, the response time also has a gradually increasing trend. The reason for this phenomenon is that as alcohol molecules increase, the orderly arrangement of CLC molecules is gradually disrupted, and then it takes longer to stabilize the change in the pitch of CLC. By comparing Fig. 6(a) and Fig. 6(b), it can be seen that the response time of the sensor to methanol is much shorter than that of ethanol. As for why this interesting phenomenon occurs, there is no detailed theoretical study yet.

The two points circled in the Fig. 6 show that the wavelength has jumped, this is because the sensor was taken out of the solution and placed in the air at that time. According to our conjecture, the reason for this phenomenon may be that the chitosan polymer network shrinks in the air, which leads to the deformation of CLCs in the network and the change of *p*. After the sensor is put into the solution, the wavelength returns to the previous initial position, indicating that the jump phenomenon has no effect on our measurement results.

The study of reproducibility of sensors: In order to study the repeatability of the sensor, we carried out repeated measurements on 0% and 15% alcohol solutions, and continuously

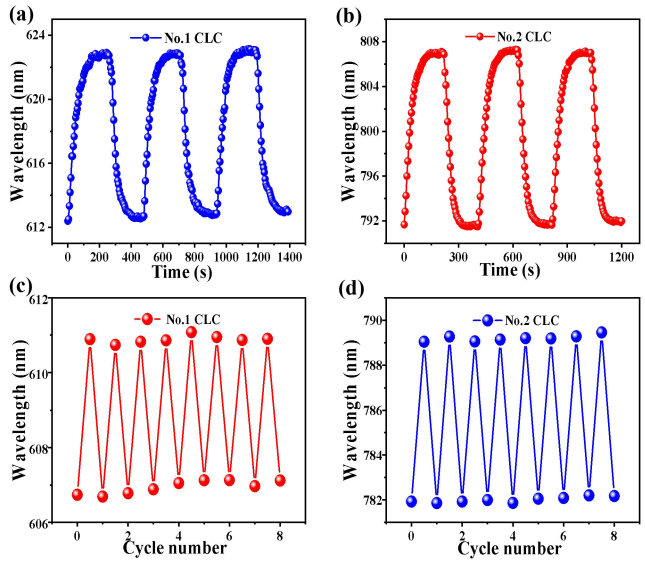

Fig. 7. Repeated dynamic responses at the ethanol concentration of 0-15%: (a) No.1 CLC and (b) No.2 CLC. Spectral responses of eight repeated measurements of the peak wavelength at the methanol concentrations of 0 and 15%: (c) No.1 CLC and (d) No.2 CLC.

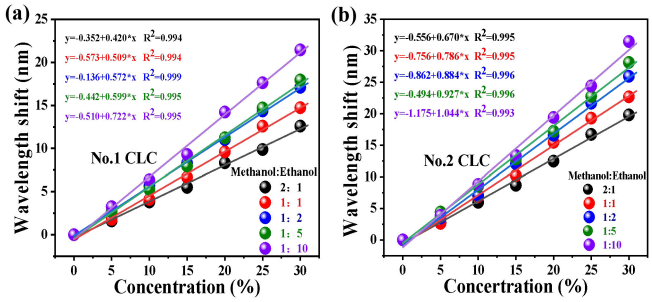

Fig. 8. Dependence of the CLCs wavelength shift on the total concentration of alcohol at different mixing ratios of ethanol to methanol: (a) No.1 CLC and (b) No.2 CLC.

monitored the movement of λ_c with a spectrometer. As shown in Fig. 7, the results of repeated measurement of No.1 CLC on ethanol in Fig. 7(a) are: when the ethanol concentration C = 0%, the maximum wavelength deviation is 0.741nm. When C = 15%, the maximum deviation is 0.275nm. In Fig. 7(b), when C = 0%, the maximum deviation of No.2 CLC is 0.234nm, and when C = 15%, the maximum deviation is 0.173nm. In Fig. 7(c), the maximum deviation of No.1 CLC is 0.437nm when methanol concentration C = 0%, and the maximum deviation is 0.34nm when C = 15%. In Fig. 7(d), the maximum deviation of No.2 CLC is 0.307nm when C = 0%. When C = 15%, the maximum deviation is 0.415nm. The results show that the sensor has good repeatability and reversibility.

The response of the sensor to the mixed solution: By controlling the ratio of methanol and ethanol and the total concentration of alcohols in the solution, a series of mixed solutions were prepared to study the response characteristics of the sensor to mixed alcohol solutions. The results are shown in Fig. 8. It can be seen from the Fig. 8 that no matter methanol and ethanol are mixed in any proportion, $\Delta\lambda_c$ increases with the increase of alcohol concentration, which is consistent with the response characteristics of single alcohol. In addition, at the same alcohol concentration, the greater the proportion of ethanol, the greater the $\Delta\lambda_c$. The reason for this phenomenon is that the polarity of ethanol is greater than that of methanol, so the contribution of the same amount of ethanol to $\Delta\lambda_c$ is greater than that of methanol. The fitting coefficient R^2 of the sensor to the mixed solution is all greater than 0.990, indicating that the response of the sensor to the mixed solution is close to linear trend.

TABLE I
DETERMINED SENSING COEFFICIENTS BY THE LEAST-SQUARES METHOD.

	No.1 CLC	No.2 CLC
A	0.331	0.345
B	48.976	76.726

According to the measurement results, the ratio and total concentration of methanol and ethanol will all affect $\Delta\lambda_c$, so $\Delta\lambda_c$ can be expressed as:

$$\Delta\lambda_c = AX + BY \tag{2}$$

Where X is the ratio of ethanol to methanol, Y is the total concentration of alcohols. A and B are the corresponding sensing coefficients of X and Y respectively. Therefore, the corresponding $\Delta\lambda_c$ of the sensor can be expressed by matrix as:

$$\begin{bmatrix} \Delta\lambda_{c1} \\ \Delta\lambda_{c2} \end{bmatrix} = \begin{bmatrix} A_1 & B_1 \\ A_2 & B_2 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} \tag{3}$$

Where $\Delta\lambda_{c1}$ represents the wavelength shift of No.1 CLC, $\Delta\lambda_{c2}$ represents the wavelength shift of No. 2 CLC, A_1 and B_1 correspond to the sensing coefficients of No.1 CLC, A_2 and B_2 correspond to the sensing coefficients of No.2 CLC. According to the experimental data, the coefficients in Eq. (2) obtained by the least square method are shown in Table I . It can be seen from Table I that the two coefficients are both positive, that means $\Delta\lambda_c$ increases with the increase of the value of ethanol/methanol and the increase of the total concentration of alcohols. Moreover, the coefficient of No.2 CLC is greater than that of No.1 CLC, indicating that the response of No. 2 CLC to alcohols is greater than No. 1 CLC. These two points are in full agreement with our experimental results. Fig. 9 shows a contour plot of $\Delta\lambda_c$ as a function of ethanol/methanol and total concentration.

It should be noted that the samples with small ethanol / methanol ratio are used in the measurement, so the coefficient obtained from the sample is only applicable to the mixed solution with small ratio. However, in the solution with large ethanol / methanol ratio, the calculated value and the actual measured value will have large errors. This problem can be solved by measuring a sample with a higher ratio of ethanol to methanol, and recalibrating the sensor's sensing coefficient in a high ethanol and low methanol environment.

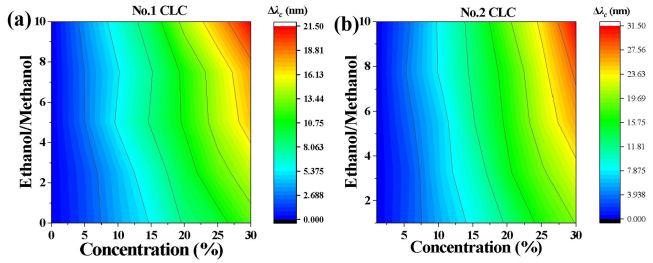

Fig. 9. Contour plots of $\Delta\lambda_c$ relative to the total concentration and ratio of ethanol and methanol: (a) No.1 CLC and (b) No.2 CLC.

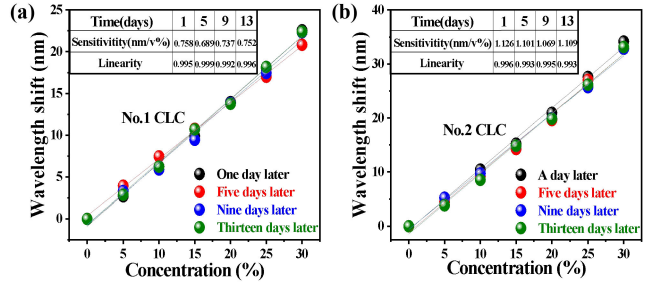

Fig. 10. The stability study of the sensor in thirteen days:(a) No.1 CLC and (b) No.2 CLC.

Study on the stability of the sensor: The response to alcohol is measured every four days in two weeks, and the fitting results are shown in Fig. 10. It can be seen from Fig. 10(a) that the maximum deviation of the sensitivity of No.1 CLC is 6.1% within thirteen days, and the maximum deviation of No.2 CLC in Fig. 10(b) is 2.9%, which proves that the sensor has very stable response characteristics to alcohol and has good time stability.

IV. Conclusion

In conclusion, an optical fiber liquid crystal sensor is designed to detect methanol and ethanol in mixed solution. Based on the principle that methanol and ethanol molecules make the pitch change differently, the proportion and concentration of methanol and ethanol in the mixed solution can be detected by monitoring the spectral shift. Through the analysis of the experimental results, the results show that methanol and ethanol molecules can make the reflection spectrum of CLCs red shift, and the sensor is more sensitive to ethanol. The size of CLCs droplet had no effect on the sensitivity. The sensitivities of the two CLCs are 0.296 nm/v% and 0.467 nm/v% to methanol, and 0.764 nm/v% and 1.133 nm/v% to ethanol, respectively. The detection range of the sensor for alcohol solution is 0.5v/v% - 30v/v%. Based on the experimental data, the linear relationship between $\Delta\lambda_c$ and ethanol / methanol and total concentration was obtained by using the least square method. The experimental results show that the sensor has present good linearity, stability and repeatability. Therefore, the optical fiber sensor based on double CLC droplets that we designed can be used to detect the methanol concentration in methanol-doped ethanol environment.

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