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# Choline chloride-based deep eutectic solvents as additives for optimizing chromatographic behavior of caffeic acid

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**Abstract**−A series of deep eutectic solvents (DESs) were prepared using glycerol and choline chloride (ChCl), and Fourier transform infrared spectrometer (FT-IR) was used to analyze the spectra of glycerol, choline chloride and DESs based on glycerol and choline chloride. Then DESs were used as the additives of mobile phase to optimize chromatographic behavior of caffeic acid in high performance liquid chromatography (HPLC). A 17-run Box-Behnken design (BBD) was employed to evaluate effect of DESs as additives by analyzing the maximum theoretical plate number. Three factors, reaction temperature (60 °C, 80 °C, 100 °C), molar ratio of glycerol and choline chloride (2 : 1, 3 : 1, 4 : 1, *n/n*), and volume percent of additives (0.05%, 0.10%, 0.15%, *v/v*), were investigated in BBD. The optimum experiment condition was that of reaction temperature (80 °C), molar ratio of glycerol and ChCl (3 : 1, *n/n*), and volume percent of additive (0.10%, *v/v*). The mean chromatographic theoretical plate number of the caffeic acid this condition was 1567.5, and DESs as additives shorten the retention time and modify the chromatogram shape, proving DESs as additives for effective theoretical plate number and column efficiency in HPLC.

Keywords: Caffeic Acid, Additive, Optimum, Maximum Theoretical Plate Number, Deep Eutectic Solvents

## INTRODUCTION

Caffeic acid has been widely investigated for its biological activity [1,2] and several biological and pharmacological properties (antioxidants [3,4], anti-inflammatory [5-8], and so on). Chemical structure of caffeic acid is shown in Fig. 1. Previous studies showed the solution of methanol-water system was used as mobile phase with $C_{18}$ column for analysis of caffeic acid in high performance liquid chromatography (HPLC), and mobile phase additives (such as phosphoric acid [9] and acetic acid [10,11]) sometimes were selected to improve chromatographic behavior and separation efficiency. However, these traditional additives are not environmentally friendly, and they are harmful to the chromatographic system. It was very necessary to find new types of environmentally friendly alternative additives.

Deep eutectic solvents (DESs) are types of green designer solvents composed of quaternary ammonium salts and hydrogen-bond donors (HBD) that show some good properties, such as low volatility, low toxicity, low cost, and high biodegradability [12-14]. DESs have attracted considerable attention in the area of synthesis, electrochemistry, materials, biochemistry, separation [15-20] in recent years. The applications of additives (such as methanol, ionic liquids, and so on) in mobile phase in HPLC have been proven to improve the peak shapes, while also affecting the column efficiency and theoretical plate number [21-24]. The DESs based on glycerol and choline chloride (ChCl) were first developed by Abbott et al. [25,26]. Glycerol is a three-carbon organic compound with a hydroxyl group on each carbon atom [27,28]. ChCl is a popular component that is a low cost, biodegradable, and non-toxic salt [29-31], making it suitable for a wide range of applications. The addition of DES in the mobile phase can be combined with response surface methodology (RSM) by changing factors (reaction conditions, volume percent of additive and so on) to obtain the optimum analysis conditions.

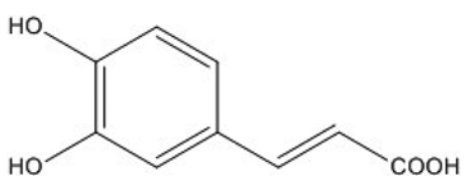


**Fig. 1. Chemical structure of caffeic acid.**

Box-Behnken design (BBD) is one type of RSM, which explores the relationships with several explanatory variables and one or more response variables [32]. It has successfully been applied to analyze the conditions in food and pharmaceutical research [33-36]. The main idea of RSM is to use a sequence of designed experiments to obtain an optimal response [37-40], and it is helpful to find the optimal condition of DESs as additives in mobile phase using RSM.

We prepared a series of DESs using glycerol and ChCl, and Fourier transform infrared spectrometry (FT-IR) was used to analyze the spectra of glycerol, ChCl and DESs based on glycerol and ChCl. Then DESs were used as the additives of mobile phase to optimize the chromatographic behavior of caffeic acid in HPLC. Moreover, three significant variables (reaction temperature, molar ratio of glycerol and ChCl, and volume percent of additives) were investigated to obtain the optimum condition of theoretical plate number using BBD.

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## MATERIAL AND METHODS

### 1. Reagents and Materials

Caffeic acid was bought from Jinsui Bio-Technology. Co., Ltd. (Shanghai, China). Choline chloride (ChCl) was bought from Guangfu Chemical Reagent Co., Ltd. (Tianjin, China). Glycerol was bought from Beichen Chemical Reagent Co., Ltd. (Tianjin, China). Acetic acid was bought from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). Methanol was bought from Jinke Chemical Research Institute (Tianjin, China). Potassium bromide (KBr) was bought from Jinke Chemical Research Institute (Tianjin, China). All the other solvents used in the experiment were HPLC or analytical grade.

### 2. Apparatus

The chromatography system consisted of LC-10ATVP pump and SPD-10AVP UV-VIS detector (Shimadzu, Suzhou, China), with the injector (20 μL sample loop). The analysis was performed on an Optima Pak $C_{18}$ column (5 μm, 150×4.6 mm, RS tech Corporation, Daejeon, Korea) and Chromatography Data System N2000 (Zheda, Hangzhou, China). The DESs were reacted in heating magnetic agitator of DF-101 (Yuhua, Gongyi, China). Distilled water (18.2 MΩ·cm) was filtered with a vacuum pump (Yukang Corporation, Shanghai, China) and a filter before use. All the samples were filtered before injection into the HPLC system.

### 3. Preparation of DESs

Glycerol and ChCl were mixed for preparation of DESs in a heating magnetic agitator with oil bath. Reaction process was investigated with different molar ratios of glycerol and ChCl (2 : 1, 3 : 1, and 4 : 1, n/n) and reaction temperature (60 °C, 80 °C, 100 °C). The DESs were formed by stirring these two components for 2 h until a homogeneous, colorless liquid was obtained. The synthesis diagram of DESs is shown in Fig. 2.

### 4. Characterization of Glycerol, ChCl and DESs

Glycerol and DESs were smeared on KBr tablets evenly, and an amount of ChCl was ground together with KBr for tablets. Then the spectra of glycerol, ChCl and DESs were analyzed by (FT-IR) (VERTEX70) (Germany Brooke Co., Ltd), with the wave numbers of 400-4,000 $cm^{-1}$.

### 5. Sample Preparation and Chromatography

The standard caffeic acid was dissolved in methanol to give a concentration of 50.00 μg·$ml^{-1}$. The analysis was performed on an HPLC system with a $C_{18}$ column. The mobile phase was methanol-water system (18/82, *v/v*) with DESs as additives. The flow rate was 0.8 ml·$min^{-1}$ and the wavelength was 330 nm.

### 6. RSM for Optimized Mobile Phase Condition

Three significant variables--reaction temperature (60 °C, 80 °C, 100 °C), molar ratio of glycerol and ChCl (2 : 1, 3 : 1, 4 : 1, *n/n*), and volume present of additives (0.05%; 0.10%; 0.15%, *v/v*))--were investigated to analyze the chromatographic theoretical plate number of caffeic acid employing a three-level, three-variables BBD.

**Table 1. Independent variables and their levels used for BBD**

| Variables | Level | | |
|---|---|---|---|
| | −1 | 0 | 1 |
| Reaction temperature (A) (°C) | 60 | 80 | 100 |
| Molar ratio of glycerol and choline chloride (B) | 2 : 1 | 3 : 1 | 4 : 1 |
| Volume percent of additive (C) (%) | 0.05 | 0.10 | 0.15 |

After determining the preliminary range of the analysis variables through single-factor test, experiments were designed to find the interaction of three variables. A 17-run BBD was applied to statistically analyze the chromatographic theoretical plate number of caffeic acid. The reaction temperature, molar ratio of glycerol and ChCl, and volume percent of additive significantly influenced the chromatographic theoretical plate number of caffeic acid determination. In Table 1, these three factors are designated as $X_1$, $X_2$, and $X_3$ prescribed into three levels, coded +1, 0, and −1 for high, intermediate and low values, respectively. The three test variables were coded according to the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X} \quad i = 1, 2, 3 \tag{1}$$

In this equation, $x_i$ is the coded value of the independent variable, $X_i$ is the actual value of the independent variable; $X_0$ is the actual value of the independent variable at the center point; and $\Delta X$ is the step change value of the independent variable. A second-order polynomial model is fitted to correlate the relationship between the independent variables and the response (the theoretical plate number) to predict the optimized conditions.

$$Y = A_0 + \sum_{i=1}^{3} A_i X_i + \sum_{i=1}^{3} A_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=1+1}^{3} A_{ij} X_i X_j \tag{2}$$

Here Y is the dependent variable (the theoretical plate number), $A_0$ is a constant, and $A_i$, $A_{ii}$ and $A_{ij}$ are coefficients that were estimated by the model. $X_i$ and $X_j$ are the levels of the independent variables that represent the linear, quadratic and cross-product effects of the $X_1$, $X_2$ and $X_3$ factors on the response, respectively. The model evaluated the effects of each independent variable on the response. The experimental design was analyzed and the predicted data were calculated by using Design-Expert software (v.7.1.6, Stat-Ease, Inc., Minneapolis, USA) to estimate the response of the independent variables. Subsequently, three additional experiments were conducted to verify the validity of the statistical experimental strategies.

## RESULTS AND DISCUSSION

### 1. Characterization of Glycerol, ChCl and DESs

FT-IR was used to analyze the characterization of glycerol, ChCl

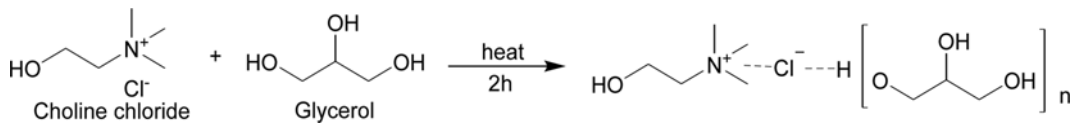


**Fig. 2. The synthesis diagram of DESs based on glycerol and choline chloride.**

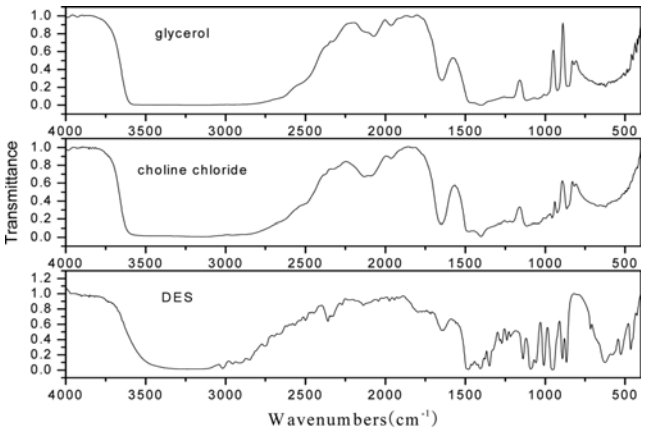


**Fig. 3. FT-IR of glycerol, choline chloride, and DES based on glycerol and choline chloride (3 : 1, *n/n*).**

and DESs, and to verify the existence of hydrogen bonds between molecules. As shown in Fig. 3, there were many differences of the FT-IR spectra among glycerol, ChCl and DESs in the fingerprint region (400-1,300 $cm^{-1}$). The sharp peaks around 405-1,305 $cm^{-1}$ show that hydrogen bonds were formed in this spectral position. ChCl and DESs displayed the characteristic peaks of -OH between 3,000 $cm^{-1}$ and 3,500 $cm^{-1}$. Also, the stretching vibration of DESs moved to the low frequency, band width and their intensity increased. Compared with glycerol and ChCl, FT-IR spectra showed the hydrogen bond of DESs was strengthened and enhanced.

**2. RSM for Optimized Mobile Phase Condition**

2-1. RSM Model Fitting and Statistical Analysis

The analysis of the caffeic acid was tested with the mobile phase (methanol-water (18/82, *v/v*)), $C_{18}$ column, flow rate (0.8 ml·$min^{-1}$). To do a quadratic regression on the model coefficients, a 17-run BBD with three factors and three levels, including five replicates at the center point, was used to fit a second-order response surface to analyze the theoretical plate number of caffeic acid. The five center point runs were carried out to measure the process stability and inherent variability, and the theoretical plate number of caffeic acid determination. The chromatographic theoretical plate number of caffeic acid determination was taken as the response. The design variables in coded units are given in Table 1. Each run was performed in duplicate, and thus, the theoretical plate number of caffeic acid was the average of two sets of experiments in Table 2, whereas the predicted values of the responses were obtained from quadratic model fitting techniques by the above mentioned software.

**Table 2. Box-Behnken experimental designs of the independent variables**

| Run | Coded variable levels | | | Theoretical plate number | |
|---|---|---|---|---|---|
| | A | B | C | Actual values | Predicted values |
| 1 | 0 | 0 | 0 | 1028.4 | 1357.5 |
| 2 | −1 | 0 | 1 | 1552.6 | 1751.4 |
| 3 | 0 | 1 | 1 | 1314.9 | 1275.4 |
| 4 | 0 | −1 | 1 | 1023.1 | 1142.0 |
| 5 | −1 | 1 | 0 | 2907.6 | 2610.6 |
| 6 | 1 | −1 | 0 | 1622.9 | 1920.0 |
| 7 | 0 | 0 | 0 | 1280.6 | 1357.5 |
| 8 | 0 | 1 | −1 | 1217.9 | 1099.0 |
| 9 | 1 | 1 | 0 | 664.2 | 1119.6 |
| 10 | 1 | 0 | 1 | 1934.3 | 1518.1 |
| 11 | 0 | 0 | 0 | 1163.2 | 1357.5 |
| 12 | −1 | 0 | −1 | 1866.7 | 2282.9 |
| 13 | 1 | 0 | −1 | 1492.0 | 1155.5 |
| 14 | 0 | 0 | 1 | 1957.8 | 1187.7 |
| 15 | −1 | −1 | 1 | 2022.3 | 1472.5 |
| 16 | −1 | −1 | 1 | 2288.0 | 1472.5 |
| 17 | 0 | −1 | −1 | 1310.3 | 1157.6 |

The predictive equation was obtained by fitting the experimental data to the BBD model in Eq. (3), which represents an empirical relationship between the response (the theoretical plate number) and the tested variables (in coded units):

$$Y=1357.52-374.55X_1-29.33X_2-7.76X_3-370.86X_1X_2+189.09X_1X_3 \quad (3)$$

**Table 3. Analysis about variance of the experimental results of the BBD**

| Variables | Sum of squares | DF | Mean square | *F* value | *P* value prob.>*F* |
|---|---|---|---|---|---|
| Model | 31686.79 | 9 | 3520.755 | 1.503312 | 0.3023 |
| A | 12086.53 | 1 | 12086.53 | 5.160776 | 0.0573 |
| B | 74.11059 | 1 | 74.11059 | 0.031644 | 0.8638 |
| C | 4.81896 | 1 | 4.81896 | 0.002058 | 0.9651 |
| AB | 6418.53 | 1 | 6418.53 | 2.740621 | 0.1418 |
| AC | 1430.201 | 1 | 1430.201 | 0.610676 | 0.4601 |
| BC | 369.0049 | 1 | 369.0049 | 0.15756 | 0.7032 |
| $A^2$ | 11039.37 | 1 | 11039.37 | 4.713654 | 0.0665 |
| $B^2$ | 18.31621 | 1 | 18.31621 | 0.007821 | 0.932 |
| $C^2$ | 1088.548 | 1 | 1088.548 | 0.464794 | 0.5173 |
| Residual | 16393.99 | 7 | 2341.998 | | |
| Lack of fit | 10917.92 | 3 | 3639.308 | 2.658339 | 0.1842 |
| Pure error | 5476.063 | 4 | 1369.016 | | |
| Correlation total | 48080.78 | 16 | | | |

**Table 4. Analysis of variables for the fitted quadratic polynomial model of theoretical plate number**

| Item | Std. dev. | Mean | C.V. % | Press | $R^2$ | $R^2_{Adj}$ | $R^2_{Pred}$ | Adeq. precision |
|---|---|---|---|---|---|---|---|---|
| Value | 48.392 | 156.746 | 30.874 | 157128.6 | 0.659 | 0.221 | 2.268 | 4.072 |

$+96.05X_2X_3+515.88X_1^2+21.01X_2^2-161.99X_3^2$

The significance of each coefficient was checked by using the *F*-test and the *p* value (Table 3). The *p* value, which was used to check the significance of each coefficient, also indicated the interaction strength between each independent variable. The ANOVA of the quadratic regression model demonstrated that the model was highly significant, with a very low probability value ($p$=0.0002). The Model *F*-value of 1.50 implied that the model was not significant relative to the noise, and there was only a 30.23% chance that a "Model *F-Value*" that was this large occurred because of noise. The lack of fit F-value of 2.66 implied the lack of fit was not significant relative to the pure error, and there was a 18.42% chance that a lack of fit F-value could have occurred because of noise. The regression coefficients and the corresponding *p* values are also shown in Table 3. The *p* values of each model, confirmed that the four coefficients ($X_1$, $X_2$, $X_3$, $X_1 \times X_1$) were all significant. Therefore, reaction temperature, molar ratio of ChCl and glycerol, and volume percent of additive to material were important factors in the determination of the caffeic acid.

The coefficient of determination ($R^2$=0.6590), the adjusted coefficient of determination ($R^2_{Adj}$=0.2206) and the coefficient of variation (C.V.=30.87%) are shown in Table 4. These values indicated that the accuracy and the general availability of the polynomial model were adequate, and the $R^2_{Pred}$ of 2.268 was in disagreement with the $R^2_{Adj}$ of 0.2206. The "Adeq. Precision" measureed the signal to noise ratio, and a ratio of greater than 4 is normally desirable. The "Adeq. Precision" of 4.072 indicated that this model could be used to navigate the design space.

2-2. Selection of Analysis Procedure

The response surface curves were plotted to investigate the interactions of the variables and to determine the optimal level of each variable for the maximum response. The optimal values of the selected variables were obtained by solving the regression equation using Design-Expert software. The 3D response surface plots are shown in Fig. 4. In Fig. 4(I), the theoretical plate number decreased at first and then increased, when molar ratio of glycerol and ChCl at the designed range from 2 : 1 to 4 : 1, and the response decreased when reaction temperature increased from 60 °C to 80 °C. In Fig. 4(II), theoretical plate number decreased at first and then increased as reaction temperature ranged from 60 °C to 100 °C, and there was a small increase about the theoretical plate number of caffeic acid determination and decreased as the volume percent of additive changing. Likewise, Fig. 4(III) showed that the theoretical plate

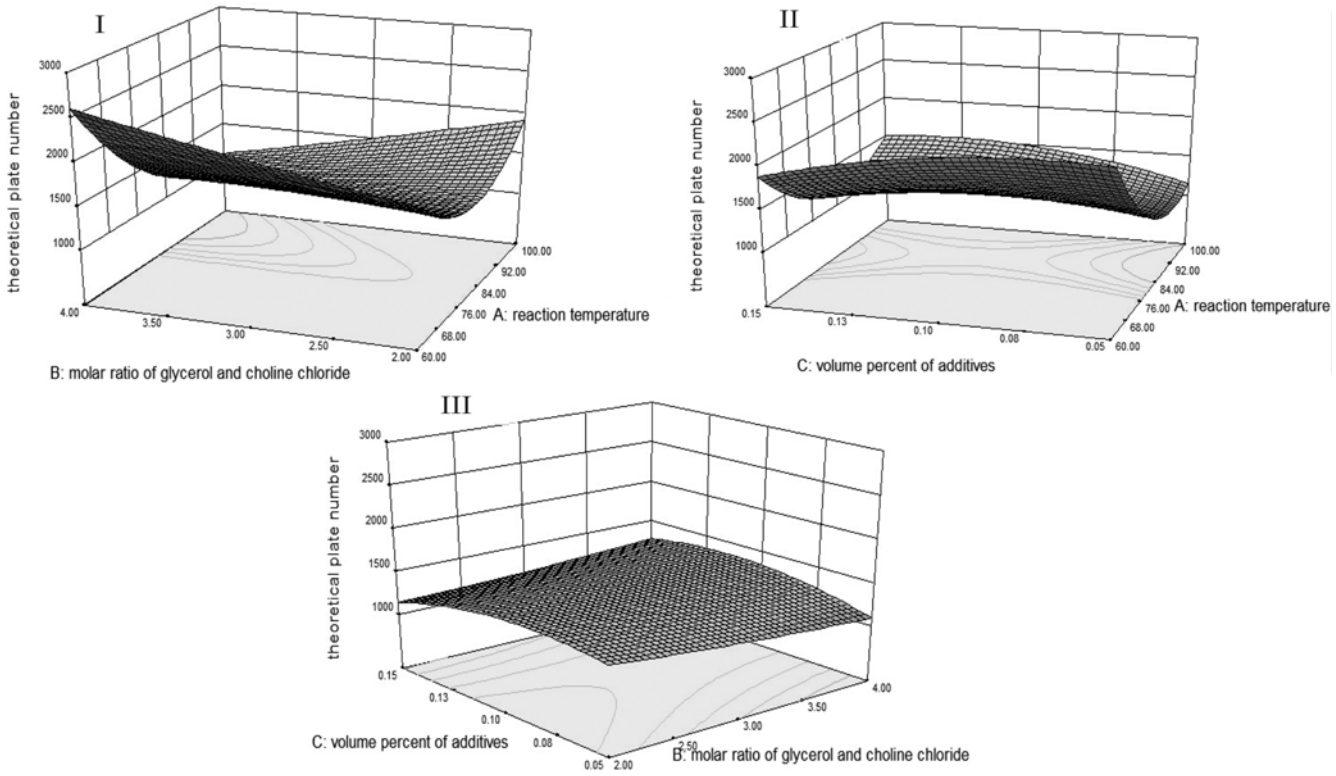


**Fig. 4. Effect of reaction time, molar ratio of glycerol and choline chloride, volume percent of additives, and their reciprocal 3D response interaction on extraction yield (Effect of reaction time and molar ratio of glycerol and choline chloride (I), effect of molar ratio of glycerol and choline chloride and volume percent of additives (II), and effect of reaction time and volume percent of additives (III).**

number increased at first and then decreased as molar ratio of glycerol and ChCl at the designed ranged from 2 : 1 to 4 : 1, and there was a small increase and then decreased as the volume percent of additive ranged from 0.05 to 0.15%.

The optimum theoretical plate number condition (reaction temperature (80 °C), molar ratio of glycerol and ChCl (3 : 1, *n/n*), and volume percent of additive 0.10%, *v/v*) for the theoretical plate number was estimated by using the model equation by solving the regression equation and analyzing the response surface contour plots. The theoretical plate number of caffeic acid that was predicted under the above conditions was 1350.72.

2-3. Changes of Chromatographic Behaviors

The optimum condition, reaction temperature (80 °C), molar ratio of glycerol and ChCl (3 : 1, *n/n*), and volume percent of additives (0.10%, *v/v*) added in the methanol-water system were tested, with the chromatogram condition (column: $C_{18}$ column, mobile phase: methanol-water (18/82, *v/v*), flow rate: 0.8 ml·min$^{-1}$, UV: 330 nm). The mean theoretical plate number was 1567.5, corresponding to the predicted value of the model equation, which confirmed that the response model was adequate for the optimization. The effects of mobile phase additives for chromatographic behavior of caffeic acid (50 μg·ml$^{-1}$) without (a) and with (b) the DESs additive and with DESs as additive are shown in Fig. 5. The result showed that DESs as additives shortened the retention time and modified the chromatogram shape, which proved DESs as additives for effective theoretical plate number and column efficiency in HPLC.

2-4. The Mechanisms of DESs as Additives

Under the optimum condition (reaction temperature (80 °C), molar ratio of glycerol and ChCl (3 : 1, n/n), and volume percent of additives (0.10%, v/v)), DESs as additives shortened the retention time and modified the chromatogram shape, proving DESs as additives for effective theoretical plate number and column efficiency in HPLC.

According to ion interaction theory, cation and anion can depend on the Coulomb attraction to make an ion pair, and they react as independent unit in solution. For DESs as additives in mobile phase, their components can work as ions and ion-pairing role at the same time. Here, the role of independent ion was bigger than ion pair. Overall, it seemed that the $[Ch]^+$ of DES played the part of cation, and $[Cl]^-$ combined with glycerol by hydrogen bonding acted as anion. $[COO]^-$ in caffeic acid can be attracted by $[Ch]^+$, and caffeic acid was easily eluted by mobile phase with DESs additives. The adsorption force of caffeic acid on the stationary phase was decreased. Retention time of target was reduced, and the separation efficiency was improved. On the other hand, $[Cl]^-$ has less localized charge, lower degree of hydration and high polarizability.

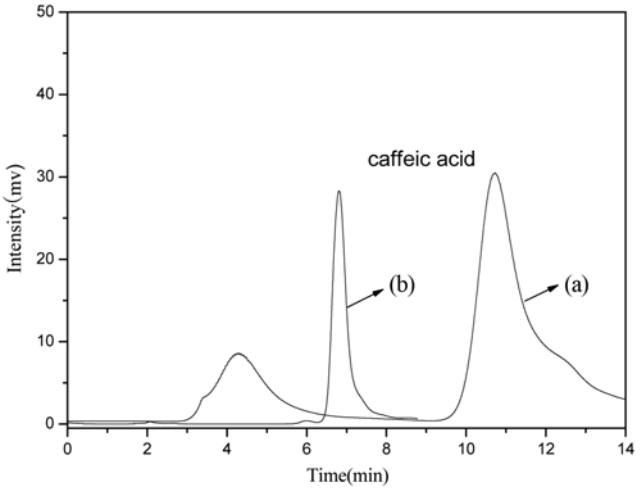


**Fig. 5. Effect of mobile phase additives for chromatographic behavior of caffeic acid (50 μg·ml$^{-1}$) without additive (a), with DESs as additive (b) (column: $C_{18}$ column, mobile phase: methanol-water (18/82, *v/v*), flow rate: 0.8 ml·min$^{-1}$, UV: 330 nm).**

## CONCLUSION

A series of DESs were prepared using glycerol and ChCl, and FT-IR was used to verify the existence of hydrogen bonds among glycerol, ChCl and DESs. BBD combined with DESs as additives was used to optimize the chromatographic behavior of caffeic acid, and they proved to be a useful tool for improving the theoretical plate number and peak shape. The optimal analysis condition was obtained (reaction temperature (80 °C), molar ratio of glycerol and ChCl (3 : 1, *n/n*), and volume percent of additive (0.1%, *v/v*)) using the BBD model equation, and the mean theoretical plate number of caffeic acid was obtained 1567.5 in these conditions.

Compared with the previous study about phosphoric acid as additive in mobile phase for determination of caffeic acid [10], DESs showed more excellent optimization performance of chromatographic behavior than phosphoric acid. Chromatographic peak shape of caffeic acid was narrowed and theoretical plate number and separation efficiency was improved. It indicated that DESs can be used to replace the acidic or alkaline additives in HPLC. This study can become the basis for later research according to optimizing chromatographic behaviors of active pharmaceutical ingredients.

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