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ORIGINAL ARTICLE

Extraction of volatile fatty acids from aqueous solution by in situ formed deep eutectic solvent with methyltrioctylammonium chloride

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Abstract

Volatile fatty acids (VFAs) such as acetic acid have a wide range of applications with high demand. Since acetic acid is well soluble in water, treating its wastewater presents a technical challenge. In this work, new hydrophobic deep eutectic solvents (DESs) were synthesized by using methyltrioctylammonium chloride (TOMAC) as hydrogen bond acceptor (HBA) and acetic acid as hydrogen bond donor (HBD). The properties of DESs were characterized by DSC, TG, and FT-IR. As HBA, TOMAC was used for in situ generation of DES to extract acetic acid from aqueous solution. The extraction efficiency reached 65.28% when TOMAC/acetic acid was 7:3 (molar ratio), which is better than that of the traditional acetic acid extractants, such as tributyl phosphate (60.46%). When metal ions such as Ca^{2+}, Mg^{2+}, and Fe^{3+} coexist in solution, the salt precipitation effect not only prevents the emulsification phenomenon but also improves the acetic acid extraction effect. For volatile fatty acids such as propionic acid, butyric acid, and valeric acid, the extraction efficiency of TOMAC was good, reaching 84.96%, 92.04%, and 95.81%, respectively. The method of using TOMAC to extract acetic acid from aqueous solutions by forming DES in situ provides a new way for the treatment of VFAs wastewater.

Keywords Acetic acid · Deep eutectic solvent · Extraction · Methyltrioctylammonium chloride · Volatile fatty acids

1 Introduction

Volatile fatty acids (VFAs) are organic acids with carbon chains of 1 to 6 carbon atoms, including acetic acid, propionic acid, n-butyric acid, isobutyric acid, pentanoic acid, and isovaleric acid, which common feature is that they are highly volatile. As a type of volatile fatty acid, acetic acid has a wide range of applications with high demand [1]. Since acetic acid is well soluble in water, treating its wastewater presents a technical challenge.

Deep eutectic solvents (DESs) are a new class of solvent formed by the interaction of two (or more) substances through hydrogen bonding [2, 3]. It is low toxic, environmentally friendly, and has a lower melting point than any single component [4]. Van Osch synthesized new deep eutectic solvents by using decanoic acid and various quaternary ammonium salts, which introduced the concept of hydrophobic deep eutectic solvents and opened a new technological platform for DES in the field of extraction [5]. Currently, the majority of studies on the use of DES for extraction and separation generally state that DES was synthesized before being used for extraction, which includes applications for the extraction of small molecules such as phenols [6, 7], organic acids [8, 9], and also metal ions [10, 11].

According to the extraction target in the mixture, the HBA or HBD is selected as the extractant and added to the mixture to generate DES in situ with the extraction target material [12]. The generated DES has a low mutual solubility with the original solvent and will not decompose in it, which is easy to be separated. Lei proposed a method for in situ generation of DES using tetrabutylammonium chloride as HBA with α-tocopherol in vegetable

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oil deodorized fractions, which obtained the product with 99.6% α-tocopherol [13]. Pang used in situ generation of DES to extract phenol from the oil phase, using choline chloride and phenol to form DES that was oleophobic and could be separated from the oil phase [14]. Zhang proposed that the choline derivative salt [$N_{1,\ 1,\ n}C_2OH$] Cl ($n = 1, 4, 6, 8$) was added to extract the phenolic compounds from the oil by forming DESs with various phenolic compounds such as 2-chlorophenol and 2-bromophenol [15]. Shishov mixed menthol with milk and DESs was formed with menthol and non-steroidal anti-inflammatory drugs (NSAIDs) such as flurbiprofen, diclofenac, and ketoprofen in milk, which resulted in the removal of antibiotics from milk [16]. Shi proposed a method to extract fluorescent whitening agent 52 (FWA 52) from aqueous solution by in situ generation of DES with hydroxybenzoate [17]. Li used tetrabutylammonium chloride to form DES with linalool in citrus essential oil to complete the extraction, and 98.7% purity of linalool could be obtained by a two-step inverse extraction method [18]. Liu added N, N-dibutylbutyramide to the aqueous solution to form a hydrophobic DES with lactic acid, which achieved the separation of lactic acid from water [19]. The above study provides guidance for in situ generation of DES to achieve extractive separation. The in situ generation of DES is a straightforward extraction technique with a high utilization rate. However, compared with synthesizing DES first and then using it for extraction, the requirements for hydrogen bond donors or acceptors that make up the DES are higher; i.e., they must meet the requirements of forming DES with the target while maintaining low mutual solubility with the original solvent for easy separation, which limits the choice of extractant [12].

The extractants traditionally used to extract VFAs include tributyl phosphate and trioctylamine, which are serious threats to human health and the environment. In this study, we used methyltrioctylammonium chloride (TOMAC) as the HBA to extract acetic acid from aqueous solutions by forming DES in situ. In order to verify that TOMAC and acetic acid can form deep eutectic solvents and to understand their related physicochemical properties, we synthesized a variety of DESs with TOMAC and acetic acid in different molar ratios and characterized their properties, such as melting point, viscosity, and thermogravimetry. Then, we used this method to examine the effect of TOMAC on the extraction of other volatile fatty acids, such as propionic acid, butyric acid, and valeric acid. In addition, the experiments also investigated the effects of the type and concentration of metal ions in the solution on the extraction of acetic acid by TOMAC.

2 Materials and methods

2.1 Materials

Acetic acid (> 99.5%) and valeric acid (> 99%) were purchased from Shanghai Titan Technology Co., Ltd. Methyltrioctylammonium chloride (> 97%, CAS NO.5137–55-3), geraniol (> 97%), and 2-heptanol (> 98%) were purchased from Shanghai Dibo Chemical Technology Co., Ltd. Calcium acetate (> 99%) was purchased from Shanghai Maclean Biochemical Technology Co., Ltd. Propionic acid (> 99.5%) purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Butyric acid (> 99%) was purchased from Shanghai Adamas Reagent Co., Ltd. Tributyl phosphate (> 99%) was purchased from Shanghai Boer Chemical Reagent Co., Ltd. Sodium hydroxide (> 96%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2 Synthesis of DES

Deep eutectic solvents were synthesized by using TOMAC as HBA and acetic acid as HBD, and the two substances were used in different molar ratios. Preparation of DES was carried out in an oil bath at 80 °C with magnetic stirring for 30 min to obtain a homogeneous clarified liquid. The DESs were left to stand at room temperature for 48 h to observe its stability.

2.3 Characterization methods

The melting point of DES was determined by differential scanning calorimeter (DSC214, NETZSCH, Germany) under nitrogen atmosphere (gas flow rate 40 mL/min) with a temperature range of – 40 ~ 60 ℃ and a temperature increase rate of 5 ℃/min. The viscosity-temperature relationship of DES was analyzed by rotational rheometer (Kinexus Lab +, ETZSCH, Germany) at room temperature to 90 ℃ and a shear rate of 2 s^{-1}. The pyrolysis temperature range of DES was determined by thermogravimetric analyzer (TGDSC 3, METTLER, Switzerland), and the sample was warmed up to 350 °C under nitrogen atmosphere (gas flow rate 30 mL/min) at a rate of 6 °C/min. The water content of the extracted phase was determined by Karl Fischer moisture meter (AKF-1 plus, Hegong, China) with methanol as the solvent. Infrared spectra of DES were analyzed by Fourier transform infrared spectra (FT-IR) (Nicolet iS5, Thermo Scientific, USA) with the test selected in ATR mode and the KBr press method in the wavelength range of 600–4000 cm^{-1}. The concentration of metal ions in the extracted solution was measured by inductively coupled plasma-atomic emission spectrometer (725 ICP-OES, Agilent, USA). A gas chromatograph (7890A GC-5975C MS, Agilent, USA) was used to analyze the purity of acetic acid obtained by distillation recovery.

2.4 Extraction experiment

An amount of methyltrioctylammonium chloride was mixed with 1 mol/L of acetic acid solution in the mol ratio of (8:2, 7:3, 6:4, 5:5, 4:6, 3:7, and 2:8.) at 25 ℃ and stirred for 15 min. After the extractant was fully mixed with the extracted solution, the mixture was left to stratify in a parting funnel for 2 h. The acetic acid concentrations of the obtained organic and aqueous phases were determined by titration with sodium hydroxide solution. The extraction rates were calculated according to Eq. (1).

$$E = \frac{C_{VFA,0}\text{-}C_{VFA,1}}{C_{VFA,0}} \times 100 \tag{1}$$

where $C_{VFA,0}$ and $C_{VFA,1}$ represent the initial acetic acid concentration and the post-extraction acetic acid concentration, respectively, mol/L.

We also evaluated the extraction ability of TOMAC for other VFAs in water, including propionic acid, butyric acid, and valeric acid. In the experiments, volatile fatty acids were configured as 1 mol/L. The molar ratio of extractant to volatile fatty acids was added as 3:7. And the experiments were carried out at ambient temperature and pressure.

3 Results and discussion

3.1 DES characterization

3.1.1 Melting point

The synthetic DES is a clear, transparent and light, yellow liquid at room temperature. The melting point of DESs is shown in Table 1**.** The low melting point is the main characteristic embodiment of DES. For deep eutectic solvents synthesized in the experiment, the DSC temperature rise curves of deep eutectic solvents formed with different molar ratios of TOMAC and acetic acid are obtained by using differential scanning calorimetry, as shown in Fig. 1a. It can be seen that among the experimentally synthesized DESs, the lowest melting point is at the molar ratio of TOMAC to acetic acid of 1:1, when the melting point is − 7.4 °C. The formation of a good hydrogen bonding network between the hydrogen bond donor and the hydrogen bond acceptor is responsible for the decrease in the melting point of DES [20, 21].

Table 1 Composition and melting point of DESs

HBA	HBD	NO	Molar ratio (HBA/HBD)	Melting point (℃)
TOMAC	Acetic acid	DES-1	4:1	0.6
		DES-2	3:2	7.9
		DES-3	1:1	− 7.4
		DES-4	2:3	6.1
		DES-5	1:4	12.3

3.1.2 Viscosity

The viscosity-temperature curves of DES-2, DES-3, and DES-4 are measured, and the results are shown in Fig. 1b. It can be seen that the viscosity of the three DESs is very high. The viscosity becomes significantly lower from DES-2 to DES-3 to DES-4. The higher the content of TOMAC, the higher the viscosity of the DES, which is also in accordance with the fluidity law observed after DES synthesis. The viscosity of three DESs could be reduced to below 100 mPa.s by increasing the temperature appropriately. The viscosity-temperature equation of the three DESs is shown in Table 2. The temperature range for which the equation applies is 30 ~ 90°.

3.1.3 Infrared spectral analysis

The infrared spectra of acetic acid, TOMAC, and DES-3 are shown in Fig. 1c. In the infrared spectrogram of acetic acid, the broad and scattered absorption peak at 3060 cm^{-1} is the stretching vibration peak of -OH [22, 23]. The strong characteristic absorption peak at 1730 cm^{-1} is the stretching vibration of C = O. The absorption peak at 1295 cm^{-1} corresponds to the stretching vibration of $-CH_3$. The results of the infrared spectrum of TOMAC are also consistent with previous reports in the literature [24]. The broad peak at 3385 cm^{-1} is most likely the telescopic vibration of the trace adsorption water O–H in TOMAC [25]. The signal peaks at 2930 cm^{-1} as well as 1465 cm^{-1} are C-H telescopic vibrations. Compared to TOMAC, the DES-3 has an absorption peak at 3340 cm^{-1}, which is the -OH stretching vibration peak. It is a broad and scattered peak. The -OH stretching vibration peak of DES-3 has shifted from 3060 (acetic acid) to 3340 cm^{-1}, i.e., a blue shift, which is caused by the hydrogen bonding between TOMAC and acetic acid [21, 26].

3.1.4 Thermogravimetric analysis

The thermogravimetric curve of DES-3 is shown in Fig. 1d. As shown by the results of DES-3 thermogravimetric analysis, there were two significant weight losses in the warming process. The weight loss of the first segment sample was 12.8%, and the weight loss of the second segment sample was 87.2%. We calculated the molar amount of material lost

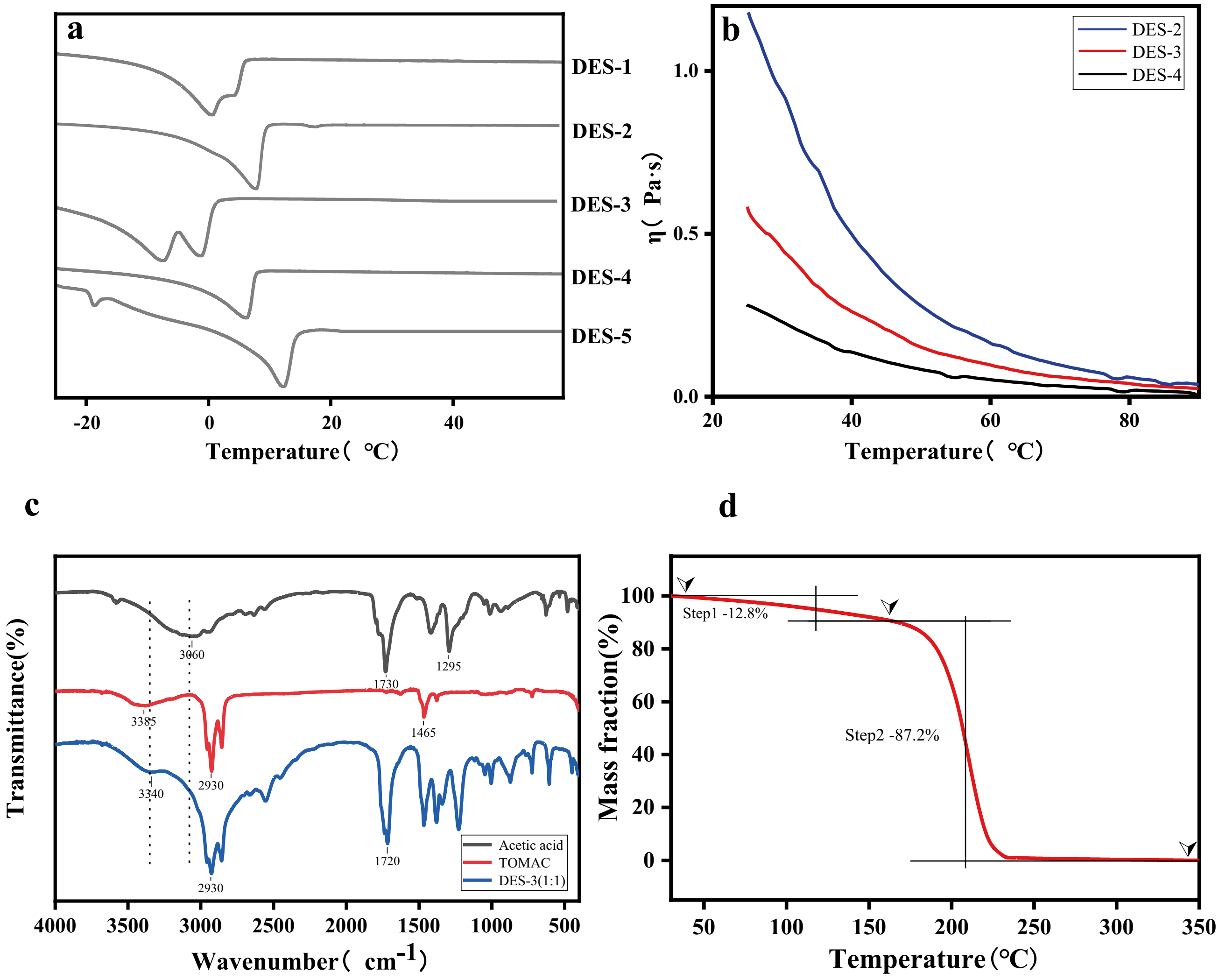

Fig. 1 **A** DSC curve of DESs. **b** Viscosity-temperature curves of DES-2, DES-3, and DES-4. **c** FT-IR spectra of acetic acid, TOMAC, and DES-3. **d** Thermogravimetric curve of DES-3

in the first segment using the relative molecular mass of acetic acid and the molar amount of material lost in the second segment using the relative molecular mass of TOMAC. It turned out that the molar ratio of the two substances was close to 1:1. According to the ratio of DES-3 ratio of TOMAC and acetic acid, combined with the theoretical boiling points of the two substances, it can be determined that the first segment is the mass loss of acetic acid and the second segment is the mass loss of TOMAC.

Table 2 Viscosity-temperature equation of DES-2 and DES-3-DES-4

DES No	Viscosity-temperature equation	R^2
DES-2	$\ln\mu = -0.0574T + 1.6238$	0.99
DES-3	$\ln\mu = -0.0513T + 0.7286$	0.99
DES-4	$\ln\mu = -0.0494T - 0.0130$	0.99

The variation pattern of the thermogravimetric curve of DES in this experiment is consistent with the thermal stability pattern of DES reported in related studies [27, 28]. At the beginning of heating, the hydrogen bonds in DES would prevent the molecules from escaping. As the temperature increases, the hydrogen bonds in DES are gradually broken. Then, the acetic acid in DES began to decompose and volatilize. However, due to the presence of hydrogen bonds, the thermal decomposition of acetic acid in DES is completed at 127 ℃, which is higher than its boiling point 118.2 ℃ [29]. As the warming continues, the TOMAC, which has a higher boiling point, also began to decompose. It can be seen that the strength of hydrogen bonding plays a decisive role in the thermal stability of DES.

The above characterization results showed that DES, a hydrophobic liquid, can be formed between TOMAC and acetic acid. Therefore, TOMAC can be applied to extracting acetic acid from aqueous solution by generating DES in situ [30].

3.2 Extraction effect of TOMAC on acetic acid

3.2.1 Effect of TOMAC dosage

The DES was generated from TOMAC and acetic acid in the solution, which forms oil phase and water phase to achieve in situ extraction. Figure 2a shows the extraction efficiency of TOMAC for acetic acid at different molar ratios. From the extraction experimental results, it can be seen that the amount of TOMAC addition is positively correlated with acetic acid extraction. The extraction efficiency reached 76.81% in the 2:8 experimental group, which organic phase to aqueous phase ratio is about 1.5:1. In addition, the 3:7 experimental group, which organic phase to aqueous phase ratio is about 1:1, was conducted to determine the water content of the extracted organic phase by Karl Fischer method. The result showed that the water content of the extracted organic phase was 17.7%.

In order to evaluate the in situ generation of DES to extract acetic acid capacity, especially compared with traditional extractants, we extracted acetic acid with geraniol [31], 2-heptanol [32], and tributyl phosphate [33], respectively. The experimental results are shown in Fig. 2b. The experiments were performed at 25 ℃, and the volume ratio of extractant to aqueous is 1. According to the comparison results, the extraction efficiency of acetic acid by the acetic acid extractants geraniol, 2-heptanol, and tributyl phosphate reported in the literature was inferior to that of TOMAC. Using the principle of DES formation, the hydrogen bonding ability combined with the ionic properties of the salt [6] resulted in a more efficient for the extraction of acetic acid by using TOMAC to extract acetic acid from aqueous solutions.

3.2.2 Effect of metal ion concentration

The effect of the presence of metal ions in solution on the ability of TOMAC to extract acetic acid was investigated. 1 mol/L acetic acid solution containing 0.05 mol/L, 0.10 mol/L, and 0.15 mol/L calcium acetate was extracted with TOMAC, respectively. The experimental results are shown in Fig. 3a. It can be seen that the concentration of metal ions in the solution becomes larger, which improves the extraction ability of TOMAC for acetic acid to some extent. In addition, we observed in the experiments of extracting acetic acid aqueous solution that there would be different degrees of emulsification in the aqueous phase as well as an emulsified layer between water and oil in the experimental group of TOMAC at the early stage after the extraction mixing (Fig. 4a). In the extraction experiments after the addition of metal ions, we also observed that the emulsification phenomenon completely disappeared and the oil–water stratification was clear (Fig. 4b).

TOMAC is a highly hydrophobic quaternary ammonium cationic surfactant which forms an emulsion when mixed with an aqueous solution of acetic acid. The ionization of calcium acetate produces Ca^{2+} and AC^{-}, which produce hydration due to the electrostatic effect. The water molecules in the hydration layer outside the emulsion are preferentially hydrated with the metal ions. The original emulsion surface hydration layer becomes weak or even disappears. The emulsification phenomenon disappears consequently. At the same time, the free water molecules in the solution are reduced. Acetic acid, which is a weak electrolyte, is released from the hydrated shell layer and facilitates its entry into the organic phase. That is the salt effect [34]. As such, the extraction

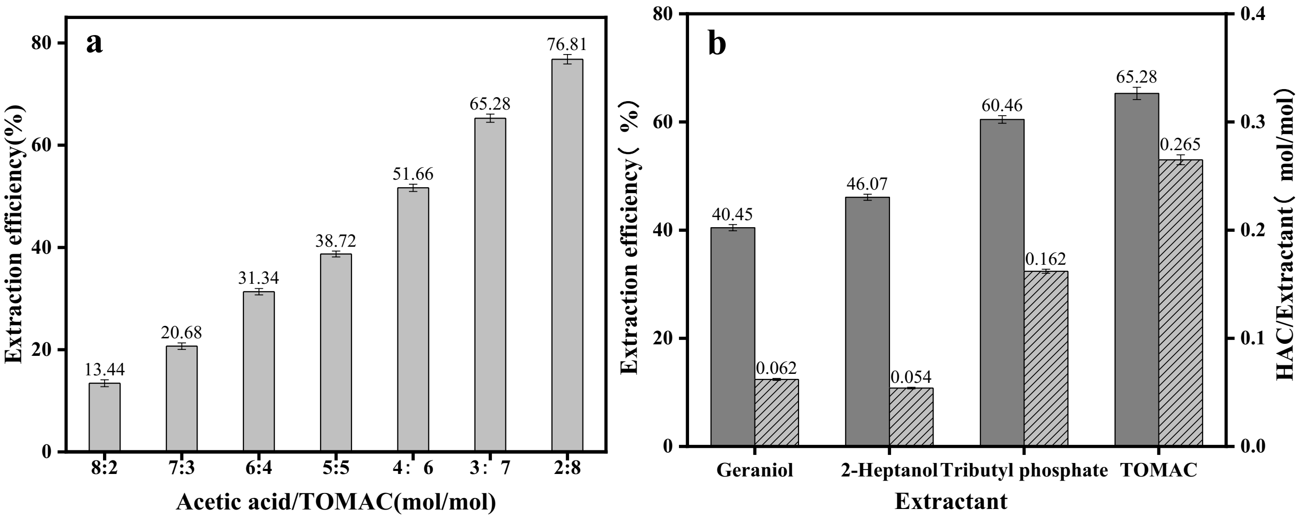

Fig. 2 **A** Effect of TOMAC dosage on the extraction efficiency of acetic acid. **b** Effect of different extractants on the extraction efficiency of acetic acid

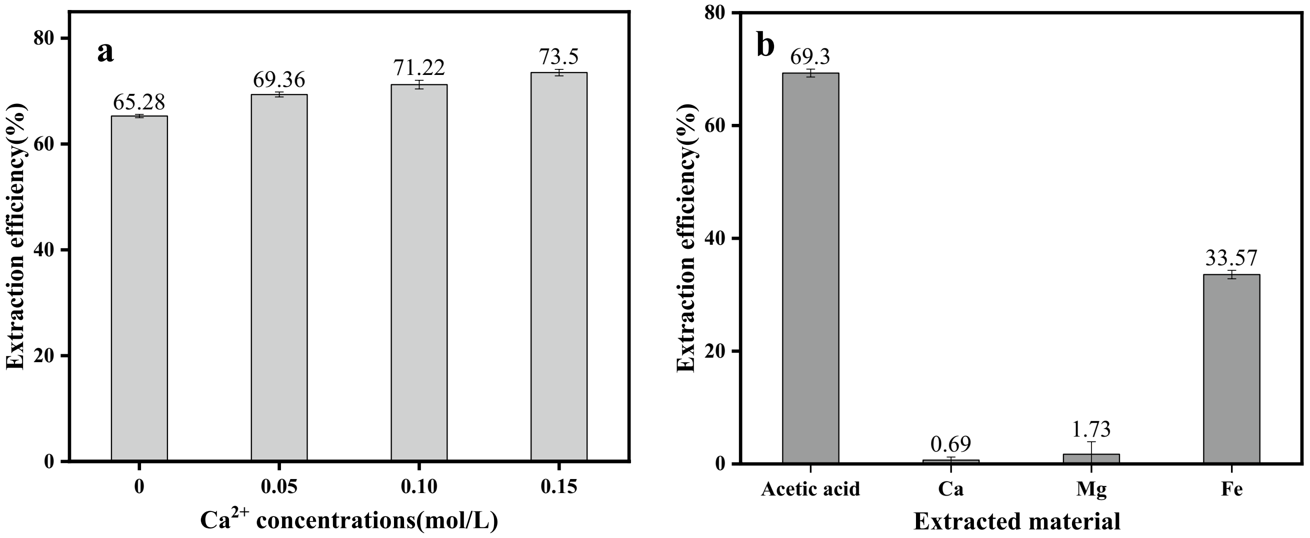

Fig. 3 **A** Effect of Ca^{2+} concentrations on the extraction efficiency of acetic acid (25 °C). **b** Extraction effect of steel slag acid leaching solution by TOMAC at 25 ℃

efficiency of acetic acid by TOMAC gradually increases when the ionic strength in the solution is increasing.

TOMAC has been confirmed to have the ability to extract some metal ions [35, 36]. In order to investigate the extraction effect of TOMAC on the co-existence of acetic acid and metal ions, TOMAC was used to extract an actual steel slag acid leaching solution. The composition of the acid leaching solution is a calcium ion concentration of 3309.3 mg/L, a magnesium ion concentration of 202.9 mg/L, an iron ion concentration of 575.8 mg/L, and an acetic acid concentration of 1.17 mol/L. The dosage of TOMAC to the acetic acid in solution is 7:3 (molar ratio). It can be seen in that the extraction effect of TOMAC on acetic acid is not affected by calcium, magnesium, and iron ions. TOMAC has a weak extraction effect on Fe^{3+}, but no extraction effect on Ca^{2+} and Mg^{2+} (Fig. 3b). The ability to extract Fe^{3+} of TOMAC has also been reported in the literature [37, 38]. Ca^{2+} and Mg^{2+} belong to strong electrolytes, which are ionized in solution. The R_4N^+ group of TOMAC is repulsive to Ca^{2+} and Mg^{2+}, so it cannot be extracted by electrostatic attraction [39], while Fe^{3+} is still not fully ionized in a weak acid environment. Therefore, TOMAC shows a selective extraction for Fe^{3+}.

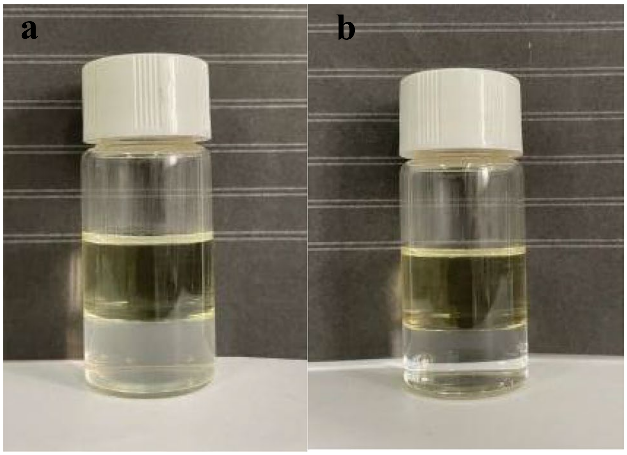

Fig. 4 Emulsification phenomenon without metal ions (**a**) and with metal ions (**b**)

3.2.3 Recovery of acetic acid

The upper organic phase obtained from the extraction was distilled at 170 ℃ atmospheric pressure. We characterized the distillation product by GC–MS, and its composition is shown in Table 3. It can be seen that the purity of acetic acid was 88.33%. By generating DES in situ, acetic acid can be recovered by distillation and can be recycled.

3.3 Effect of TOMAC on the extraction of VFAs

The concentration of acetic acid, propionic acid, butyric acid, and valeric acid to be extracted was 1 mol/L, and the dosage of TOMAC fixed to the amount of acid in water was 7:3 (molar ratio). The results of extraction of acetic acid, propionic acid, butyric acid, and valeric acid are shown in Fig. 5. The ability of TOMAC to extract volatile fatty acids gradually increases as the hydrocarbon chain of volatile fatty acids grows. And it can be seen that the extraction efficiency for both butyric and valeric acids has exceeded 90%. This can be explained by introducing

Table 3 Composition of recovered acetic acid by GC–MS

Substance	Content (%)
2,5-Furandione	0.23
Octanal	4.35
Cyclooctane	0.55
Methyl nonanoate	2.66
Acetic acid	88.33
1-Undecanethiol	0.12
Pentafluoropropionic acid	0.12
Cyclopropane	0.49
2-Methyldodecenoic acid	0.17
8-Pentadecanone	0.35
Caprylic acid	0.15
1-Methylcyclohexene	0.27
Bis(2-ethylhexyl) phthalate	0.1
Heptanal	0.11
Butane	0.38
n-Hexadecanoic acid	0.13
α-(4-Isobutylphenyl)propanal oxime	0.17

solubility parameters [40]. The solubility parameters of TOMAC, water, and VFAs are shown in Table 4, which is calculated by the Van Krevelen group contribution method [41]. It can be seen that the difference of dispersion (δ_d) between VFAs and water is small and the biggest differences exist mainly in the hydrogen bonding (δ_h). As the alkane chain grows, the dispersion of VFAs gradually increases, and the polarity (δ_p) gradually decreases, which also gradually approaches the dispersion and polarity of TMOAC. The difference between dispersion and polarity with water increases, which means that the solubility of VFAs in water gradually becomes worse, and thus easy to be extracted.

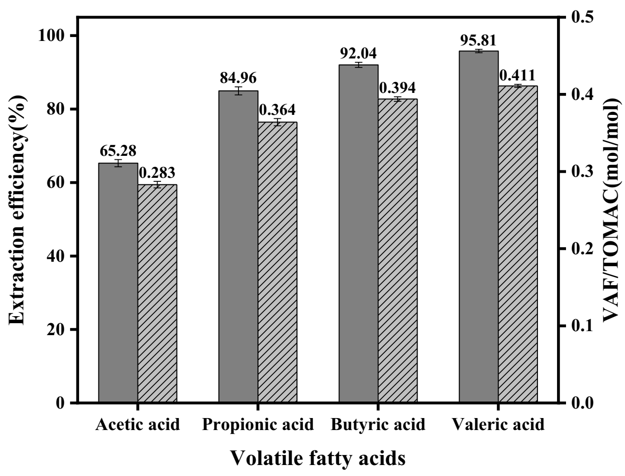

Fig. 5 Extraction effect of volatile fatty acids by TOMAC at 25 ℃

Table 4 Solubility parameters of water, VFAs, and TOMAC

	Dispersion (δ_d) ($MPa^{1/2}$)	Polarity (δ_p) ($MPa^{1/2}$)	Hydrogen bonding(δ_h) ($MPa^{1/2}$)
Water	15.5	16	42.3
Acetic acid	14.5	8	13.5
Propionic acid	16.3	5.6	11.6
Butyric acid	16.2	4.6	10.4
Valeric acid	16.2	3.9	9.6
TOMAC	17.1	2.1	3.4

4 Conclusion

In this study, a variety of new DESs were synthesized by TOMAC and acetic acid. In the extraction experiments, the extraction efficiency reached 76.81% when TOMAC/acetic acid = 8:2 (molar ratio). In the phase ratio of 1:1, TOMAC showed a better extraction effect on acetic acid. The presence of metal ions Ca^{2+}, Mg^{2+}, and Fe^{3+} in the solution did not affect the extraction of acetic acid by TOMAC. TOMAC basically has no extraction effect on Ca^{2+} and Mg^{2+}, while it has an extraction effect on Fe^{3+}. The extraction efficiency of Fe^{3+} by TOMAC was about 33% when extracting acetic acid. For volatile fatty acids such as propionic acid, butyric acid, and valeric acid, the longer the alkane chain, the better the extraction effect of TOMAC on them. The extraction effect on valeric acid was up to 95.81% for valeric acid. TOMAC shows excellent extraction performance for VFAs by in situ formation of DESs, which provides a new direction for the separation of VFAs from aqueous solutions. This method can be applicable for treating VFAs wastewater, even if the wastewater contains metal ions.

Author contribution Linchao Zhu (First Author): Investigation, Writing-original draft.

Lin Wang: Conceptualization, Resources.

Peiqing Yuan: Data curation.

Xinru Xu: Validation.

Jingyi Yang (Corresponding Author): Project administration, Supervision, Writing-review editing.

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Ethical approval This declaration is not applicable.

Competing interests The authors declare no competing interests.

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