Form CO₂-responsive microemulsion for extracting ethanol from water by triethylamine

Wenting Du, Ling Lyu *, Xin Zhang, Hongwei Xu
College of Chemical Engineering and Chemistry Technology, Southwest Petroleum University, Chengdu 610500, China

*Corresponding author e-mail: 200631010031@swpu.edu.cn

Abstract. Compared with traditional distillation separation, extraction of ethanol from ethanol water could reduce the energy consumption. But emulsion generated in the process of strong mixing caused difficulty of separation of two phases. A new method of extraction ethanol could realize the efficient mass transfer and the complete separation of two phases. The microemulsion system was constructed by adding TEA (triethylamine) into ethanol water, and then ethanol was extracted from the water by 2-ethyl-1-hexanol. The extraction efficiency was close to the theoretical value, and the extracted emulsion could be demulsified under the action of CO₂. The method did not require strong stirring, and had low energy consumption and high extraction efficiency. It solved the problem to separate the emulsion generated in the process of ethanol extraction.

Key words: extraction; demulsification; The CO₂ response; ethanol water.

1. Introduction
Biological fermentation was the main method for the production of fuel ethanol [1]. The commonly method for separating ethanol from fermentation broth in industry was pervaporation coupled method, which included two steps [2]. The first step was to obtain 22% (wt%) of ethanol aqueous solution by pervaporation in situ separation. In the second step, ethanol and water were separated by distillation to obtain ethanol products with a purity of more than 99% [3]. Distilation of ethanol water directly needed huge energy consumption [4]. Reducing the energy consumption of the second step was the key step to reduce the energy consumption of the whole fermentation process for ethanol production.

Solvent extraction using low cost extractants might provide a more energy-saving method to recover ethanol [5]. 2-ethyl-1-hexanol could be used as a kind of ideal extractant to extract ethanol from aqueous solution because of better distribution coefficient and separation factor, non-toxic for fermented liquid, the cheap price and high boiling point [6, 7]. However, water, ethanol and 2-ethyl-1-hexanol could form O/W emulsion easily under the stirring condition during the extraction process. Critical conditions, such as centrifugation of 276 G, should be applied for complete separation [8]. A better method should be found to separated ethanol from water to enhance separation of two phases and mass transfer.

Microemulsion is a kind of stable system that can be formed without strong agitation. Compared with emulsion, it has smaller droplets, larger mass transfer surface area and lower energy consumption. However, mechanical demulsification of the microemulsion usually could not be achieved. If the
microemulsion can be rapidly demulsified, the mass transfer and the separation can be simultaneously improved in the extraction process. In 2018, Lu et al. reported that a microemulsion was destroyed under the action of CO2. It led to the demulsification of heavy oil emulsion [9]. Chen et al. reported a CO2-responsive superamphiphile was designed to form switchable O/W microemulsions of rapid switching responses [10].

To reduce energy consumption and improve both the mass transfer efficiency and the separation efficiency, 2-ethyl-1-hexanol was used for extraction separation of ethanol water. TEA was added into ethanol water to form microemulsion. After ethanol-water-TEA microemulsion formed, droplets of 2-ethyl-1-hexanol were added into the microemulsion to achieve full mass transfer, then CO2 was bubbled into the emulsion to realize separation of the extract phase and the raffinate phase. TEA in the raffinate phase was restored and cycled after bubbling N2. This method of constructing microemulsion could realize the extraction and separation of co-surfactant such as ethanol in water, which had high extraction efficiency, green environmental protection, and a good application prospect.

2. Experimental

2.1. Reagents and instruments
Chemical reagents included: 2-ethyl-1-hexanol, TEA, ethanol; deionized water. Diameters of oil droplets in the emulsion were detected by a laser particle analyzer. Concentrations of ethanol in the oil phase were detected by gas chromatography test.

2.2. Experimental Principle
As shown in figure 1, TEA was added into ethanol water to form microemulsion and 2-ethyl-1-hexanol was added for extraction. The extracted microemulsion was bubbled CO2 to achieve two-phase separation. The oil phase consisted of ethanol and 2-ethyl-1-hexanol, while the water phase consisted of ammonium salt formed for protonation of TEA, unextracted ethanol and water. N2 was introduced into the aqueous phase for deprotonation. The ammonium salt in the upper layer was deprotonated and reduced to TEA, while the lower layer was unextracted ethanol aqueous solution. The unextracted ethanol aqueous solution could be mixed with the fresh solution. TEA could be recycled to form microemulsion for the next extraction. The construction of microemulsion to achieve separation of ethanol and water had low energy consumption and green environmental protection.

Fig. 1 Schematic diagram of the extraction ethanol from water.

3. Results and discussion

3.1. Ternary phase diagram
At 25°C, 10g of ethanol was added to the beaker to prepare ethanol and TEA solutions with mass ratio of 5:1 to 1:5 respectively. Then, pure water was added into the different proportions samples until the
system became turbidity from clarification. The amount of water was recorded. Ethanol, water and TEA were fixed as three vertices of the ternary phase diagram, and the phase diagram of the system was drawn according to the content of each component when the system reached the phase boundary. In the figure 2, the lower part of the curve was the multiphase region, while the upper part of the curve was the monophase region. The area of the monophase region was large, while the area of the multiphase region was small. The corresponding composition of the points falling in the monophase region could form the microemulsion system.

3.2. Conductivity in the extraction procession

Weighed 10g TEA and 2g ethanol in a 100mL beaker at 25℃, then mixed them evenly. Placed them in a constant temperature magnetic stirrer, and dropped pure water into it while stirring. Data were recorded for adding each 0.5g water.

It could be seen from the figure 3 that the electrical conductivity of the mixed system presented three different trends with the increase of water content. First conductivity changed was no obvious with the increase of water, because the addition of water droplets formed a water-in-oil droplets in the ethanol/TEA system. But at the beginning, the water content was low let to the formation of droplet number was limited. The interaction of conductivity between droplets had a slight increase but change was not obvious. With the addition of water, the droplets of water-in-oil microemulsion gradually increased in the system and the exchanges of ions and charges between them intensified. It made the electrical conductivity of the system increase linearly. The microemulsion was water-in-oil and clear. When the amount of water in the system was 6g, 2-ethyl-1-hexanol was added to extract ethanol gradually. With the further increase of 2-ethyl-1-hexanol content, the electrical conductivity of the system showed a downward trend. The increasing of 2-ethyl-1-hexanol content leads to decrease of ethanol in the water. Consequently, the effective ion concentration decreased and the electrical conductivity decreased in the water.
3.3. pH value in the extraction process

Fig. 4 showed the change of pH value of the microemulsion in the extraction process. At 25℃, 10g of TEA and 2g of ethanol were weighed in a 100mL beaker and mixed evenly. Pure water was added while stirring, and the changes of pH value were recorded. With the increase of water content, the pH of the microemulsion began to rise significantly. With the increase of water content, the amine ion concentration in the water increased so that the pH increased. After 6g of water being added, TEA2-ethyl-1-hexanol was started to be added. With the increase of 2-ethyl-1-hexanol content, the pH value showed a downward trend. This was due to the increase of ethanol transfer to 2-ethyl-1-hexanol. The increase of relative water content led to the decrease of pH value.

3.4. The mixed state of the system in the extraction process

Judged the state of the system in the extraction process by dropping Sudan red III in the system. As shown in figure 5, under 25 ℃, 20% ethanol water and TEA could form microemulsion in figure 1(a). In figure 1(b), the microemulsion state could maintain after adding 2-ethyl-1-hexanol. When 2-ethyl-1-hexanol was continued to be added into the water/ethanol/TEA/2-ethyl-1-hexanol microemulsion, the microemulsion changed into emulsion in figure 1(c). After bubbling CO2, emulsion was separated into two layers. The upper layer was ethanol and 2-ethyl-1-hexanol, the bottom layer was ammonium salt and ethanol water not being extracted.
3.5. Extraction efficiency

Calculation method of experimental extraction efficiency was as follows:

$$\eta_1 = \frac{m_1}{m} \times 100\%$$

Where, \( \eta_1 \) was the experimental extraction efficiency of ethanol; \( m_1 \) was the mass of ethanol in the 2-ethyl-1-hexanol solution after extraction; \( m \) was the total mass of ethanol in the original microemulsion, units of \( m_1 \) and \( m \) were g.

Theoretical extraction efficiency was calculated by the following formula:

$$\eta_2 = \frac{nK_D}{1 + nK_D}$$

Where, \( \eta_2 \) was the theoretical extraction efficiency of ethanol; \( n \) was the volume ratio of 2-ethyl-1-hexanol to ethanol water in the extraction process; \( K_D \) was the equilibrium distribution coefficient of ethanol in the oil phase and the water phase, and the unit was g/g.

Experimental and theoretical extraction efficiency of ethanol were shown in Table 1. It could be seen from the table that the extraction efficiency were 8.8% by experiment and 10% by calculation. The results showed that the experimental extraction efficiency was close to a single equilibrium level.

| Extraction efficiency | ethanol (g) | TEA (g) | 2-ethyl-hexanol (g) | water (g) | \( K_D \) | \( \eta \) (100%) |
|-----------------------|------------|---------|---------------------|----------|-------|----------------|
| \( \eta_1 \)         | 3          | 15      | 1.5                 | 5        | -     | 8.8            |
| \( \eta_2 \)         | 3          | 15      | 1.5                 | 5        | 0.65  | 10.0           |

4. Summary

To extract ethanol from water and realize separation of oil phase and water phase, TEA was added into ethanol water then microemulsion formed firstly. Secondly, extraction occurred in the microemulsion enabled the extraction efficiency to better achieve the theoretical value because the smaller droplets improved the mass transfer area. The microemulsion state could be maintained after adding 2-ethyl-1-hexanol but the microemulsion was transformed into emulsion after adding the excess 2-ethyl-1-hexanol. At last, extract phase and raffinate phase could be separated through adding CO\(_2\). Mass transfer and separation in the extraction of ethanol could be enhanced through this way.
References

[1] Carlos, A., Cardona, O. Fuel ethanol production: Process design trends and integration opportunities. Bioresource Technology. 98 (2007), p. 2415-2457.

[2] Peng, P., Shi, B., Lan, Y. A Review of Membrane Materials for Ethanol Recovery by Pervaporation. Separation Science and Technology. 46 (2010), p. 234-246.

[3] Leland, M. V. 2005. A review of pervaporation for product recovery from biomass fermentation processes. Chem Technol Biotechnol. 80 (2005), p. 603-629.

[4] King, C. Factors Influencing Solvent Selection for Extraction of Ethanol from Aqueous Solutions. Ind. Eng. Chem. Process Des. Dev. 23 (1984), p. 109-115.

[5] Saeed, L. A, Ali, K. Comparative solvent extraction study of silver(I) by MEHPA and Cyanex 302 as acidic extractants in a new industrial diluent (MIPS). Hydrometallurgy 160 (2016), p. 38-46.

[6] Egan BZL, D. D., McWhirter, D. A. Solvent Extraction and Recovery of Ethanol from Aqueous Solutions. Ind. Eng. Chem. Res. 27 (1988), p. 1330.

[7] Bazua, C. D., Wilke, C. R. Ethanol Effects on the Kinetics of a Continuous Fermentation with Saccharomyces cervisiae. Bioeng. Symp. 7 (1977), p. 105.

[8] Offeman, R. D., Stephenson, S. K., Robertson, G. H., et al. Solvent Extraction of Ethanol from Aqueous Solutions. I. Screening Methodology for Solvents. Ind. Eng. Chem. Res. 44 (2005), p. 6789-6796.

[9] Liu, D., Suo, Y., Zhao, J., et al. Effect of Demulsification for Crude Oil-In-Water Emulsion: 1 Comparing CO2 and Organic Acids. Energy & Fuels. 32 (2018), p. 757-764.

[10] Chen, X.; Ma, X.; Yan, C.; Sun, D. Yeung, T.; Xu, Z. CO2-responsive O/W microemulsions prepared using a switchable superamphiphile assembled by electrostatic interactions. Journal of Colloid and Interface Science. 534 (2019), p. 595-604.