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# Stability and performance study of newly developed emulsion prepared with polymeric rubber emulsifier and using the emulsion for nicotine extraction

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ABSTRACT

A stable water-in-oil (W/O) emulsion was prepared using polymeric additive as emulsifier instead of surfactant Span 80 (sorbitan monooleate) and kerosene as the organic membrane phase. The rubber emulsifiers were prepared using polybutadiene–styrene rubber (PBSR) or polybutadiene rubber (PBR) as the polymeric additive in this work. It was found that the rubber emulsifier acted like a surfactant in the emulsification process. The factors of influence of the W/O emulsion stability were investigated. The emulsion stability and mass transfer efficiency were assessed by measuring the concentration of nicotine in the internal strip and the external feed phase, respectively. The rheological behavior of W/O emulsion prepared with the rubber emulsifiers was also compared with that of W/O emulsion prepared with Span 80. It showed that the W/O emulsions prepared with the rubber emulsifiers were non-Newtonian when it dispersed in a continuous aqueous solution at low stirring speed. Applying the W/O emulsion for extraction of nicotine from real tobacco samples was carried out through dispersing it in the tobacco nicotine extractant aqueous solution. The results showed that nicotine was almost transferred from the feed to strip phase in 2 min and the efficiency of nicotine mass transfer was exceeded 99%.



## 1. Introduction

Since emulsion liquid membranes (ELMs) invention by Li [1], ELMs have been used to separate a variety of solutes from aqueous solutions due to its high separation efficiency in recent years, such as the removal of dyes [2–6], phenols [7–11], amines, and metals [12–16] in wastewater, as well as the extraction of cholesterol from blood [17]. In addition, ELMs can be used as delivery systems in cosmetic and/or pharmaceutical fields for the controlled release of hydrophilic or lipophilic compounds [18]. Although the ELMs technique has several advantages over other physicochemical techniques, it still suffered from the long-term operation failure due to the instability of the emulsion.

Generally, W/O emulsion is prepared using water and a low-HLB (hydrophilic–lipophilic balance) surfactant, such as Span 80 solution, in oil. To extract target solute, W/O emulsion must be dispersed in a continuous sample solution formulating a water–oil–water (W/O/W) system. In the W/O/W system, the tiny oil droplets contain fine aqueous stripping agent (internal phase) droplets acting as a selective barrier. Target solute in the sample solution (external feed phase) is transferred across the oil membrane into the internal strip phase trapped them inside. During an extraction process, the formulation of W/O/W should be maintained and not be destroyed. Therefore, a long-term stability of W/O emulsion plays an important role in the extraction operation. In previous applications, such as removal of dye and metals from wastewater, W/O emulsion is stability in long-term operations as long as the targeted species is present at low concentrations in the external feed phase. Unfortunately this is not extent to the extraction of alkaloids from herbal medicines where external feed phase is complex bio-matrix solution and not only target species contained in the sample solution [19]. In these cases, a good enough stability of W/O emulsion is crucial, because the complex bio-matrix solution as external feed phase will result in a failure of formulating a suitable the W/O/W system.

A high stability of W/O emulsion can be prepared through increasing concentration of surfactant in oil (membrane phase) [20,21] and/or increasing viscosity of the membrane phase [22,23]. However, these emulsions produce another effect of mass transfer reducing due to the viscosity of W/O emulsion increasing [24]. In recent years, some studies show that the effect of emulsion

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viscosity on mass transfer rate can be improved through adding polymeric additive in the membrane phase during preparation of W/O emulsion. Applied the W/O emulsion with added isobutylene in the extraction of benzoic acid, Hopper found that the solute transfer rate negligibly changed, compared to the emulsion without added polymeric additive, despite an increase in fluid viscosity of more than a 100-fold [25]. From then, numerous similar studies have been reported [26–30]. These studies showed the membrane phase (composed of kerosene, and surfactant, polymeric additive) had a structure of facilitating solute transport in a similar manner [31]. From this point of view, polymeric additive is a key ingredient in the membrane phase. However, the effects of polymeric additive in the membrane phase are not clear. In addition to this, it is not clear either that a stable W/O emulsion if could be prepared by only using polymeric additive instead of Span 80. In our best knowledge, few studies on the preparation of the W/O emulsion without adding Span 80 and investigating the stability of it are carried out. Therefore, this paper intends to fill this gap.

We have firstly prepared W/O emulsions using two kind of polymeric additive PBSR and PBR in the absence of Span 80 and secondly, studied their stability and performance in W/O/W system. The rheological behavior of W/O emulsion with polymeric additive was also compared with that of W/O emulsion without polymeric additive. The emulsion stable factors, such as the polymeric additive concentration in membrane phase, the ratio of oil to water, the emulsification agitation speed, time and disperse time were investigated in the part of 3.1–3.5. The factors of influence on the mass transfer rate, including the strip phase acid concentration, the solute concentration in feed phase, the selection of carrier, the carrier concentration and amount in the membrane phase were discussed in the part of 3.6–3.9. Based on these studies, an optimal process condition achieved and applied it for extraction of nicotine from real tobacco sample solution.

## 2. Experimental

### 2.1. Materials and reagents

The commercial PSBR (1500 series) and PBR (mean molecular weight 540 kDa) were purchased from the market (manufacturer: Yanshan, Bejing) without further purification. The kerosene (boiling point range of 200–240 °C) and nicotine ethanol solution (*V*:*V* = 1:1) were obtained from the manufacturers (Yanshan, Bejing and Yulan, Baoding). Span80 (Beko Chemical Co. Ltd., China) was purchased from a local chemical store (Xinhua, Baoding). Acetic acid (36%) and other chemical regents used in experiment, such as methylene dichloride and ethyl acetate were all of reagent grade except special noted, were purchased from Kemiou Chemical Company (Tianjin, China). Sulfuric acid with different concentration aqueous solution, sodium hydroxide solution (5%) and the double distilled water used throughout all the experimental process were prepared in our laboratory.

### 2.2. Polymeric emulsifier

Polymeric emulsifier was prepared by dissolving PBSR or PBR in kerosene. Briefly, PBSR (5 g) was dissolved in 150 mL of kerosene in room temperature under stirring as emulsifier 1, abbreviated *E*1; PBR (5 g) was dissolved in 150 mL of kerosene in room temperature under stirring as emulsifier 2, abbreviated *E*2.

### 2.3. Preparation of emulsion

The emulsion (W/O) was prepared by mixing the aqueous internal strip phase with the organic membrane phase using a high-speed mixer for a fixed mixing time. The organic membrane phase was composed by kerosene and emulsifier (*E*1 or *E*2); the internal strip phase was sulfuric acid aqueous solution. The parameters including the volume ratio of emulsifier to kerosene in the membrane phase, the volume ratio of the strip phase to the membrane phase, the concentration of sulfuric acid in the strip phase, the emulsification time, and the agitating speed were listed in Table 1. Total of 33 samples were tested.

### 2.4. Emulsion extraction

The W/O/W extraction system was set under a magnetic stirrer at 150 rpm. The nicotine solutions of different concentrations were used as the external feed phase. The prepared W/O emulsion (10 mL) was dispersed in 40 mL of external feed solution (nicotine solution) in a conical flask under magnetic stirring to make the W/O/W double emulsions for emulsion extraction. Extracting for a while, magnetic stirrer was tuned off and the W/O/W was layered by gravity. The lower external feed phase was removed for determination of its volume and pH. The concentration of nicotine in the external feed phase was determined by automatic polarimeter according to a standard curve. The standard curve showed the optical rotation values as a function of the concentration of nicotine solution, which showed a linear relationship with a good correlation coefficient in the nicotine concentration range from 100 to 1600 μL/L ($Y = 3.0877X \cdot 10^{-4} + 6.64526 \cdot 10^{-4}$, $R^2 = 0.9978$). Each experiment was performed at least triplicates and the mean values were calculated.

### 2.5. Determination of mass transfer rate

After removal of external feed phase from W/OW emulsion, W/O emulsion was alone remained. The W/O underwent a demulsification process for separation of oil and water. The demulsification of W/O emulsion was performed by heating the emulsion with magnetic stirring (120 rpm). Organic membrane oil phase and internal strip phase were separated and removed respectively to determine their volume and pH. The mass transfer rate was obtained through determination of concentration of nicotine in the aqueous internal strip phase by measuring its degree of polarization. Each measurement was performed at least triplicates and the mean values were calculated.

## 3. Results and discussion

### 3.1. W/O emulsion stability

The stability of W/O emulsion can be assessed by an emulsion breakage ($\lambda$), which is defined through the following formula

$$\lambda = \frac{\Delta V}{V_{i0}} \times 100 \quad (1)$$

where $\Delta V$ is the change of volume of the internal strip phase during the extraction process and $V_{i0}$ is the initial volume of the internal strip phase. The bigger value of $\lambda$ is, the more magnitude of W/O rupture. The measuring volume of the internal strip phase, however, is easy brought in error in process due to its small volume. Therefore, an apparent emulsion breakage $\lambda_{app}$ is usually used to determine the stability of emulsion instead of $\lambda$ [32]. The $\lambda_{app}$ is defined as $\lambda_{app} = \frac{\text{Amount of target species permeated in feed solution}}{\text{Total of the target species amount in strip solution}} \times 100$ that is

$$\lambda_{app} = \frac{C_e V_{et}}{C_{i0} V_{i0}} \times 100 \quad (2)$$

where $V_{et}$ is the volume of the external feed phase solution at that time, $C_{i0}$ is the initial concentration of solute in the internal strip

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