W/O high internal phase emulsions (HIPEs) stabilized by a piperazinyl based emulsifier

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1. Experimental

1.1 Materials

NaCl, Erucic acid (EA), 1-Amino-4-methylpiperazine (AMPA), 3-(dimethylamino)-1-propylamine (DMAPA), 1-methylpiperazine (MP) and 1-(2-aminoethyl) piperazine (AEP), kerosene, heptane, cyclohexane, petroleum ether, $CDCl_3$ and Dicyclohexylcarbodimide (DCC) were purchased from Aladdin Chemical Reagent Company without further purification.

1.2 EA/AMPA synthesis

AMPA (11.5 g, 0.1 mol) and DCC (21.6 g, 0.105 mol) were placed in a three-necked flask with 80 mL of dichloromethane (DCM) and chilled to 0 °C. EA (33.8 g, 0.1 mol) was dissolved in 20 mL of DCM and placed in a dripping funnel and introduced into the round bottom flask slowly over a period of 30 minutes. Then, the mixture was reacted at 35 °C for 6 h. After that, 20 ml water was poured into the mixture and stirred for 1 h. The white precipitate was removed and the product was wash with water for three times. Finally, the organic phase was concentrated on a rotary evaporator at 50 °C. The product with the color of light yellow was collected to give 91.1% yield.

1.3 Structure characterization

The raw materials and EA/AMPA were analyzed by Fourier transform infrared spectroscopy. The samples were mixed with KBr powder and then pressed into sheets for testing (Figure S1). To further confirm the chemical structure of EA/AMPA was dissolved in $CDCl_3$ and then analyzed by nuclear magnetic resonance spectroscopy (1H NMR, Bruker) to determine the product structure.

1.4 Preparation of W/O High Internal Phase Emulsion

The designed amount of EA/AMPA was dispersed in water to get white dispersion (Figure S2). The crude oil or kerosene colored by oil red was added to the dispersion. Then, the mixture was stirred by mechanical agitator (OS-40Pro, DLAB) with paddle impeller. Water bath was used to control the temperature.

1.5 Micromorphology of the HIPEs

The micrographs of the prepared emulsion were measure by optical microscope (CX40, Sunny Optical Technology Company) at room temperature.

1.6 Viscosity Analysis

The viscosity of the W/O emulsion as well as crude oil was carried out using a Brookfield DV2T viscometer.

2. Results

The spectrum of EA. -CO**OH** (3428 cm^{-1}), **-CH=CH-** (3005 cm^{-1}), **-CH$_2$** (2854-2930 cm^{-1}), -**CO**OH (1712 cm^{-1})

The spectrum of AMPA. -**N-H** (3432 cm^{-1}), **-CH$_2$** (2854-2930 cm^{-1}), **-N-H** (1654 cm^{-1})

The spectrum of EA/AMPA. -CO**NH$_2$** (3236 cm^{-1}), **-CH=CH-** (3005 cm^{-1}), **-CH$_2$** (2854-2930 cm^{-1}), -**CO**NH (1614 cm^{-1})

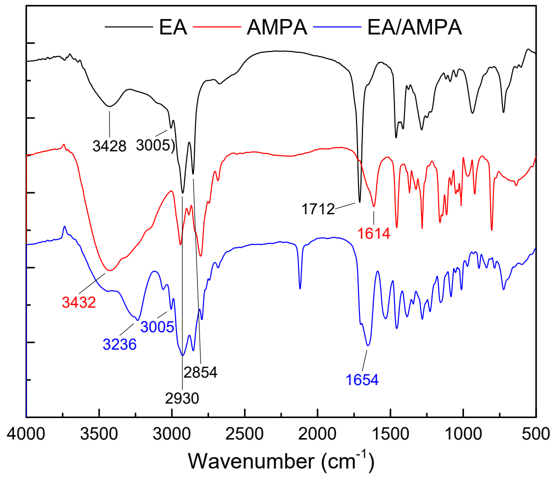

Figure S1. The FTIR spectrum of EA/AMPA

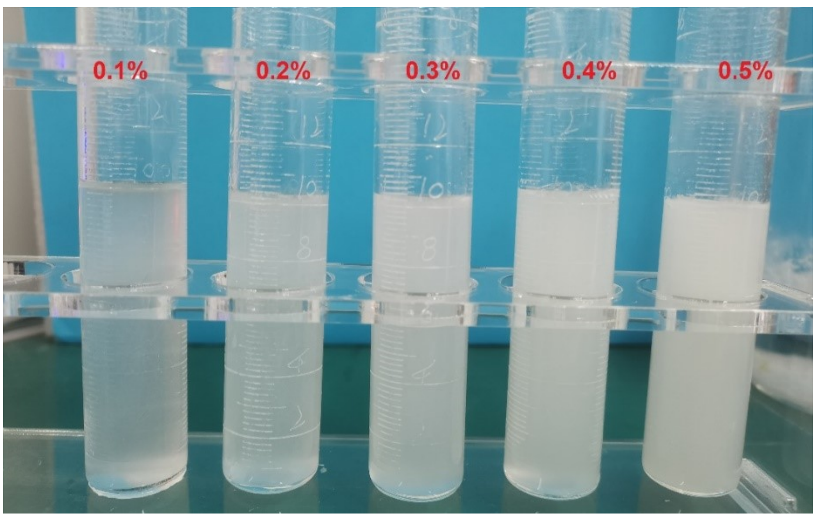

Figure S2 The digital photos of EA/AMPA dispersed in water

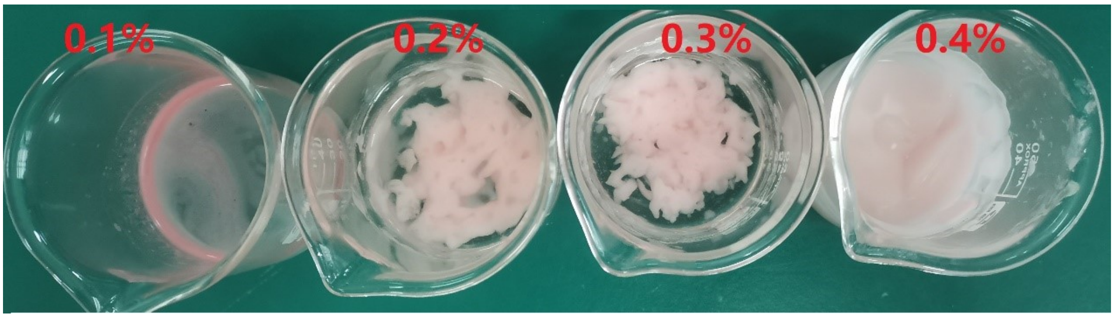

Figure S3 The digital photos of the HIPEs with 98% water content at different EA/AMPA concentration

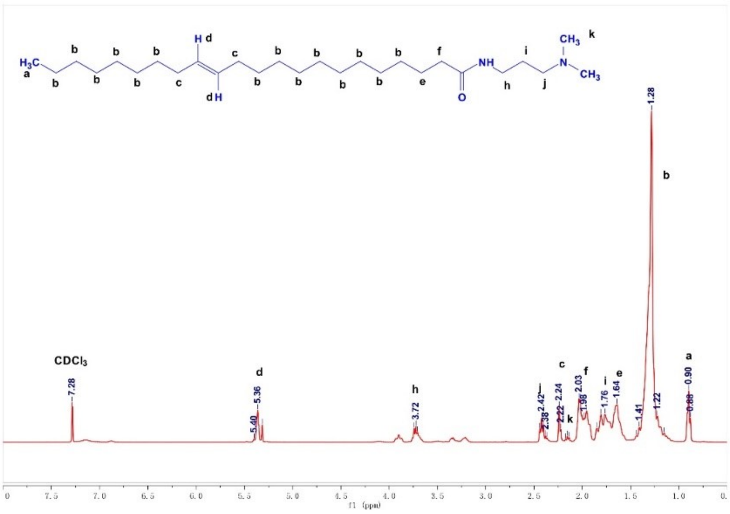

Figure S4 The ^{1}H-NMR spectra of EA/DMAPA

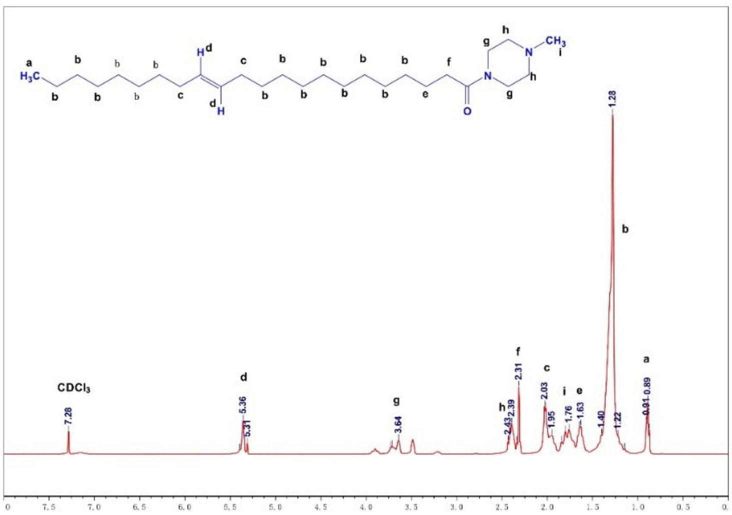

Figure S5 The ^{1}H-NMR spectra of EA/MP

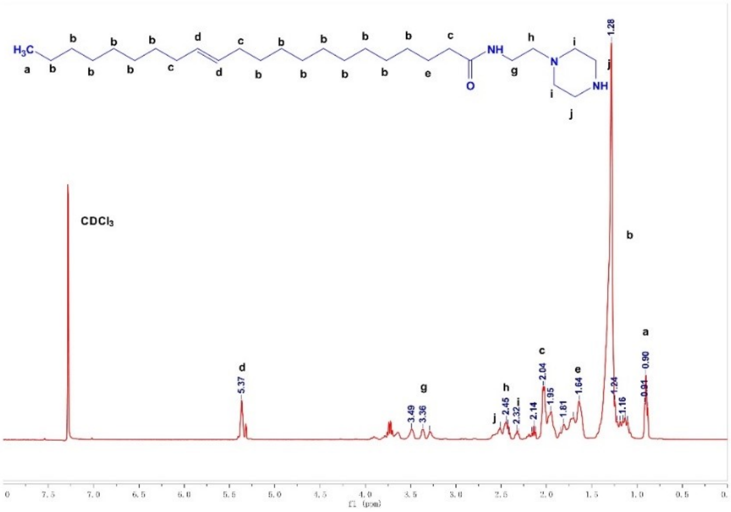

Figure S6 The ^{1}H-NMR spectra of EA/AEP

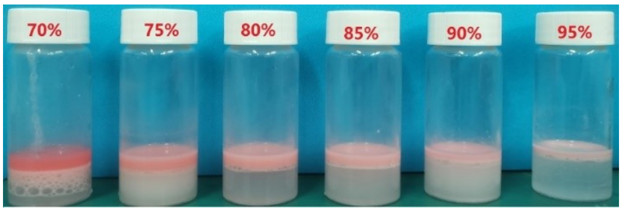

Figure S7 The digital photos of emulsions by using EA/DMAPA

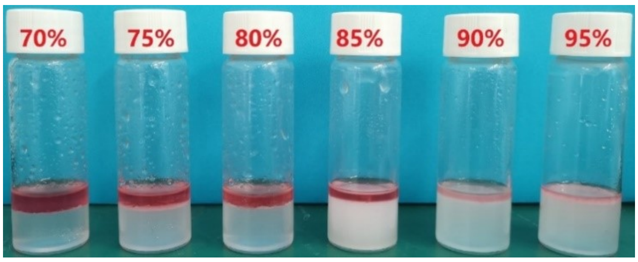

Figure S8 The digital photos of emulsions by using EA/MP

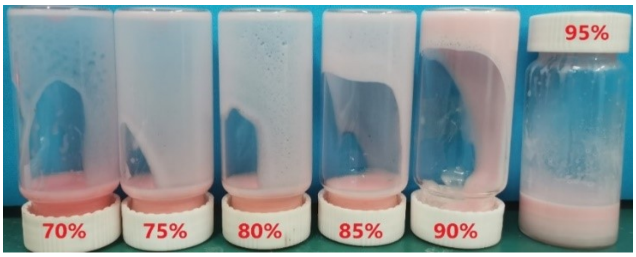

Figure S9 The digital photos of emulsions by using EA/AEP

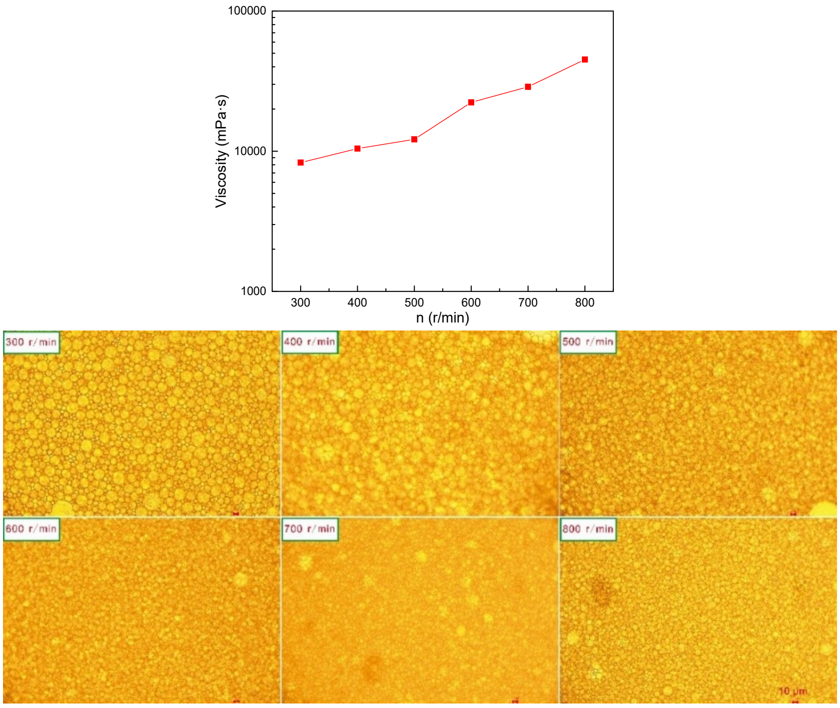

Figure S10. Micrographs of W/O emulsion with different rotation speed (water content, 90%; EA/AMPA, 0.4%; mixing time, 15 min)

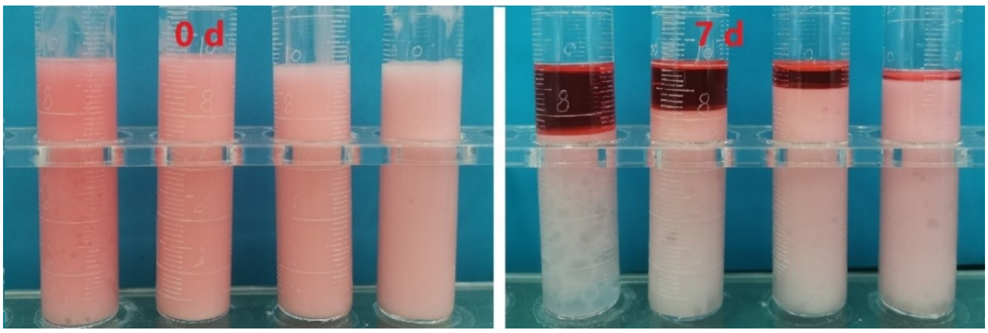

Figure S11. The stability of the emulsions (the internal phase fraction: 70%, 75%, 80%, 85%)

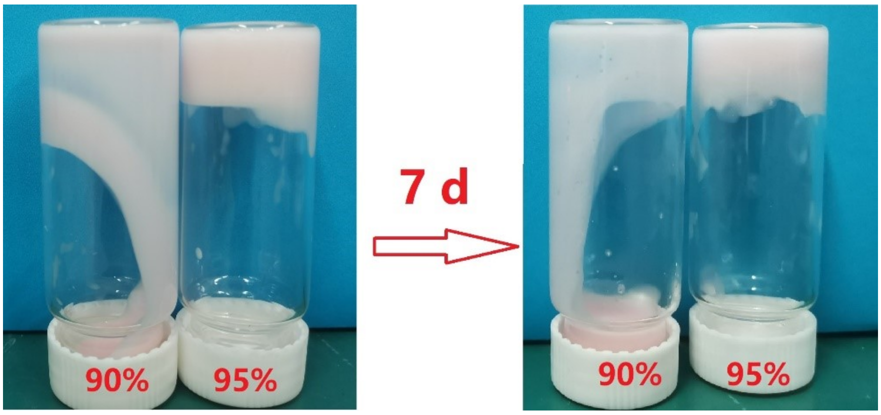

Figure S12. The digital photos of the HIPEs over time

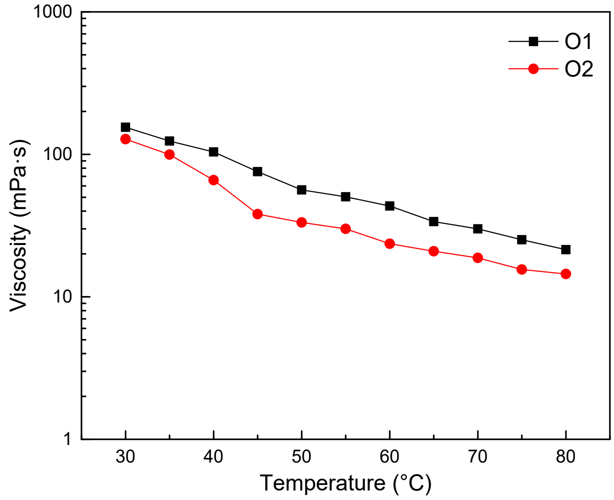

Figure S13. The effect of temperature on the viscosity of the used crude oil

Table S1. The parameters of the used crude oil

Oil	Viscosity (mPa·s)	Density (g/cm^3)	Acid Value (%)	Resins (%)
O1	158.3	0.866	0.33	41.2
O2	128.6	0.863	0.31	40.6

Table S2. The parameters of the used saline water

Na^+ (g/L)	Ca^{2+} (g/L)	Cl^- (g/L)	Salinity (g/L)
3.46	0.07	5.41	8.94