Electronical Supplementary Information

Cyclodextrins: from solute to solvent

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Experimental Details

Preparation of the solvent

The solvent was prepared by mixing RAMEB and levulinic acid (30:70 %wt). The mixture was then stirred at 60 °C until the formation of a clear homogenous liquid. The water content of the prepared solvent was determined using Karl Fisher titration method (Mettler Toledo DL31).

Density and viscosity measurements

Density measurements were conducted using a U-shaped vibrating-tube densimeter (Anton Paar, model DMA 5000 M) operating in a static mode. The factory calibration was used and verified before and after each measurement with air and tri distilled degassed water.

The viscosity was determined using a falling-ball-based microviscosimeter (Lovis 2000 M/ME from Anton Paar). The temperature was controlled to within 0.005 K and measured with an accuracy better than 0.02 K. A capillary tube of 1.8 mm diameter, previously calibrated as the function of temperature and angle of measurement with reference oils, was used for the measurements.

DSC

DSC experiments were carried out using a Q1000 DSC (TA Instruments, New Castle DE) at a temperature range going from -100 °C to 40 °C and at a thermal scanning rate of 5°C.min^{-1}. The samples were encapsulated in aluminum pans (sample weight ~ 10-15 mg), sealed with hermetic lids and characterized. Experiments were performed under nitrogen flow (50 mL.min^{-1}).

Static Headspace-Gas Chromatography (SH-GC)

All measurements were carried out with an Agilent G1888 headspace sampler coupled with a Perkin Elmer Autosystem XL gas chromatography equipped with a flame ionization detector and a DB624 column using nitrogen as carrier gas. The GC column temperature was fixed at 160 °C. Solubility of AN in RAMEB:Lev was determined using the method described by Moufawad et al[1].

NMR

All NMR experiments have been recorded on a Bruker Avance III spectrometer operating at 400 MHz for the proton nucleus, equipped with a multinuclear z-gradient BBFO probe head. In all experiments, the probe temperature was maintained at 303 K and standard 5 mm NMR tubes with D_2O insert were used.

The ^{1}H spectra were recorded with the following acquisition parameters: time domain 55 K with a digital resolution of 0.20 Hz, relaxation delay: 2 s, and 16 scans.

2D-ROESY spectrum of RAMEB/AN complex in RAMEB:Lev solvent was acquired with a mixing time of 800 ms during spin-lock, using off resonance pulse program troesyph, and States-TPPI method with a 2048 K time domain in F2 and 512 experiments in F1 with 200 scans.

2D-DOSY spectra have been performed using the bipolar longitudinal eddy current delay (BPPLED – Bipolar Pulsed Field Gradient Longitudinal Eddy Delay) pulse sequence. In each DOSY experiment, a series of 16 spectra with 20 K points were collected, with 16 scans. The pulse gradients have been incremented in 16 steps from 2 to 98 % of the maximum gradient strength in a linear ramp. Diffusion times (Δ) and gradient pulse durations (δ) were optimized for each experiment in order to achieve a 95 % decrease in resonance intensity at the largest gradient amplitude; typically, δ between 3 and 1.4 ms, Δ between 300 and 75 ms. After Fourier transformation, phase and baseline correction, the diffusion dimension of the 2D-DOSY spectra was processed by means of MestRenova software (version 11.0.2). The diffusion constants were calculated by Peak Heights Fit method with 128 points in diffusion dimension.

Figures

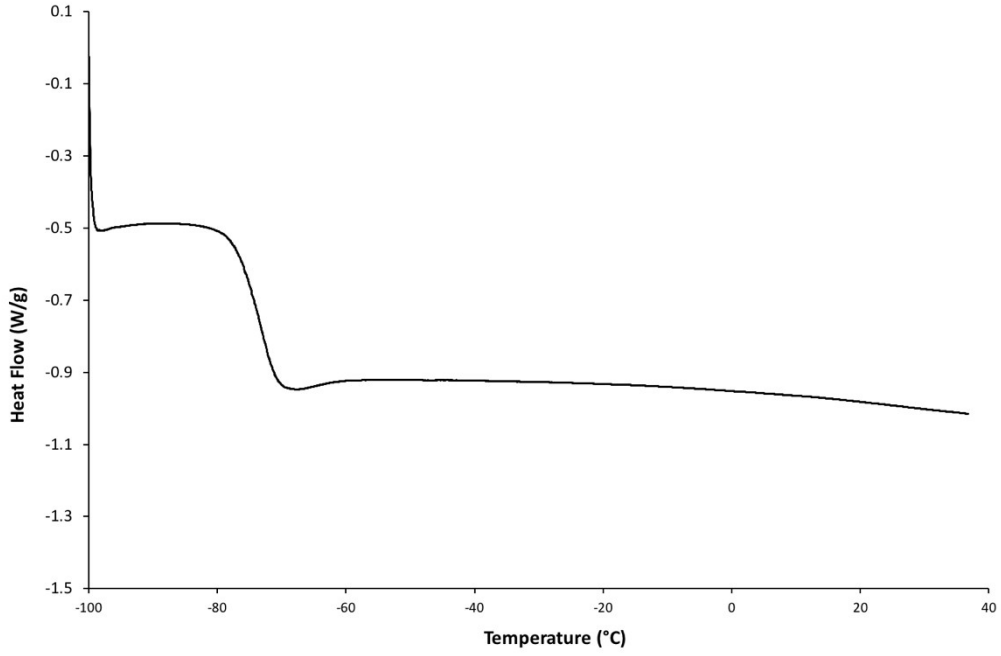

Figure S1. DSC curve of the new supramolecular solvent RAMEB:Lev.

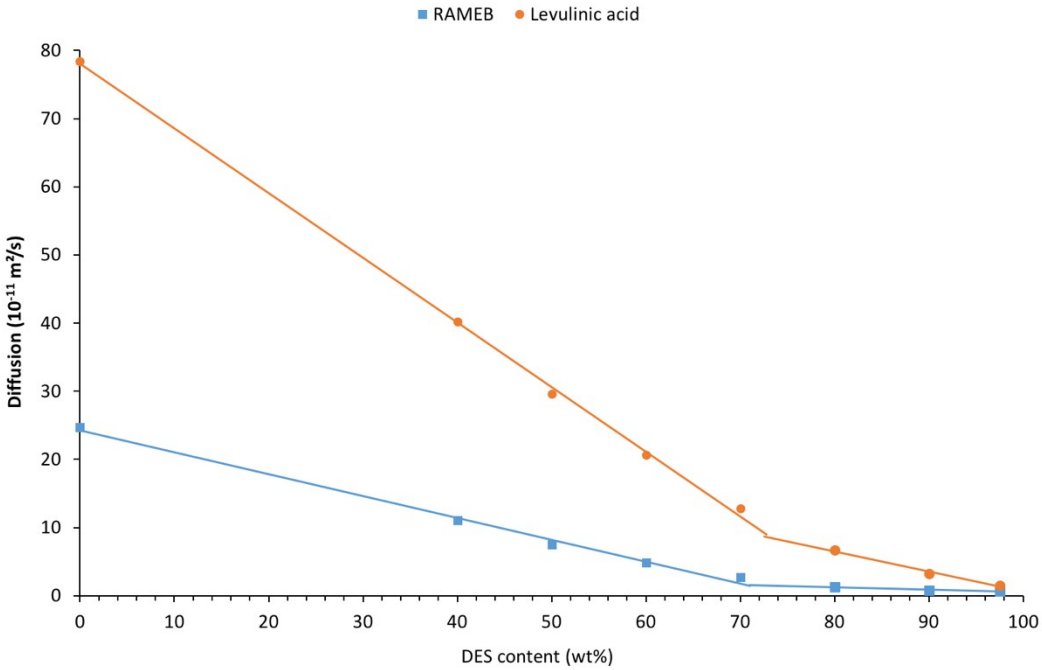

Figure S2. Plot of diffusion coefficients obtained from NMR spectroscopy versus DES content (in wt%) in DES-H_2O binary mixtures.

Table

Table S1. Experimental values of the density (ρ) and viscosity (η) of RAMEB:Lev between 303.15 and 333.15 K.

T (K)	ρ (kg m^{-3})	η (mPa s)
303.15	1184.5	212.9
313.15	1176.4	111.2
323.15	1168.2	63.6
333.15	1159.8	39.3

Reference

1. T. Moufawad, L. M. Moura, M. Ferreira, H. Bricout, S. Tilloy, E. Monflier, M. C. Gomes, D. Landy and S. Fourmentin, *ACS Sustain. Chem. Eng.*, 2019, **7**, 6345–6351.