Electronic Supplementary Information (ESI)

T/K	X1
438.21	0.1600
421.19	0.2117
411.40	0.2478
398.57	0.3195
389.21	0.4004
384.53	0.4379
380.37	0.4872
376.60	0.5241
373.38	0.5666
370.69	0.5999
367.42	0.6483
364.78	0.6889
362.50	0.7273
360.41	0.7639
358.23	0.8098
356.67	0.8410
355.31	0.8749
354.53	0.8939
352.95	0.9431
352.12	0.9746
351.44	1.0000

Table S.1 Boiling temperatures (*T*) and liquid mole fractions (x_1) for the system ethanol (1) + [emim][EtSO₄] (2).

Table S.2 Antoine coefficients A, B, and C for pure compounds.

Compound	A	В	С
ETBE	6.83000	1682.812	3.242
Ethanol	7.23710	1592.864	-46.966
[emim][EtSO ₄]	0	100	0

Table S.3 Density (ρ), dynamic viscosity (η) and refractive index (n_D) of the pure components of the ternary system studied in this work, at 298.15 K and atmospheric pressure.

Component	$\rho/\text{g·cm}^{-3}$		η / mPa·s		n_D	
	Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
ETBE	0.73551	0.7350 1	0.371	Not found	1.37298	1.3730 ²
Ethanol	0.78522	0.78493 ³	1.077	1.0826 ³	1.35923	1.35941 ³
[emim][EtSO ₄]	1.23882	1.2296 ⁴ 1.2423 ⁵	100.4	100.7 ⁶	1.47889	Not found

¹ J. H. Oh and S. J. Park, J. Chem. Eng. Data, 1998, 43, 1009.

² R. Reich, M. Cartes, J. Wisniak and H. Segura, *Fluid Phase Equilib.*, 1999, **154**, 99.

³ J. A. Riddick, W. B. Bunger and T. Sakano, *Organic Solvents. Physical Properties and Methods of Purification*, John Wiley, New York, 4th edn., 1986.

⁴ J. Z. Yang, X. M. Lu, J. S. Gui and W. G. Xu, *Green Chem.*, 2004, **6**, 541.

⁵ M. Krummen, P. Wasserscheid and J. Gmehling, J. Chem. Eng. Data, 2002, 47, 1411.

⁶ J. Jacquemin, P. Husson, A. A. H. Padua and V. Majer, *Green Chem.*, 2006, **8**, 172.

Equipment for the measurement of the physical properties:

Density. Densities were measured, with a precision of 1×10^{-5} g·cm⁻³, in a vibrating U-tube Anton Paar DMA 60 density meter with a DMA 602 measuring cell attached. Temperature was controlled by means of a Heto Therm ultrathermostat, and measured with a precision of ±0.001 K using a CTK100 Anton Paar precision thermometer.

Viscosity. Measurements of viscosity were carried out in an Ubbelohde viscometer. Measurements of the liquid flow times through it were performed by a Lauda Processor Viscosity System PVS1 with a resolution of 0.01 s. Temperature was kept constant using a Lauda clear-view thermostat D 20 KP with a through-flow cooler DLK 10 attacher, with a thermal stability of ± 0.005 K.

Refractive index. An ATAGO RX-5000 refractometer was used to determine the refractive indices of the substances with a precision of 4×10^{-5} . Control of the temperature was carried out with a Techne thermostat (±0.01 K).