

Supplementary

# An Innovative Vortex-Assisted Liquid-Liquid Microextraction Approach Using Deep Eutectic Solvent: Application for the Spectrofluorometric Determination of Rhodamine B in Water, Food and Cosmetic Samples

Sofia Kakalejčíková <sup>1</sup>, Yaroslav Bazel <sup>1\*</sup>, Van Anh Le Thi <sup>1</sup> and Maksym Fizer <sup>2</sup>

<sup>1</sup> Department of Analytical Chemistry, Institute of Chemistry, Pavol Jozef Šafárik University in Košice, 040 01 Košice, Slovakia; sofia.kakalejcikova@student.upjs.sk (S.K.); van.anh.le.thi@student.upjs.sk (V.A.L.T.)

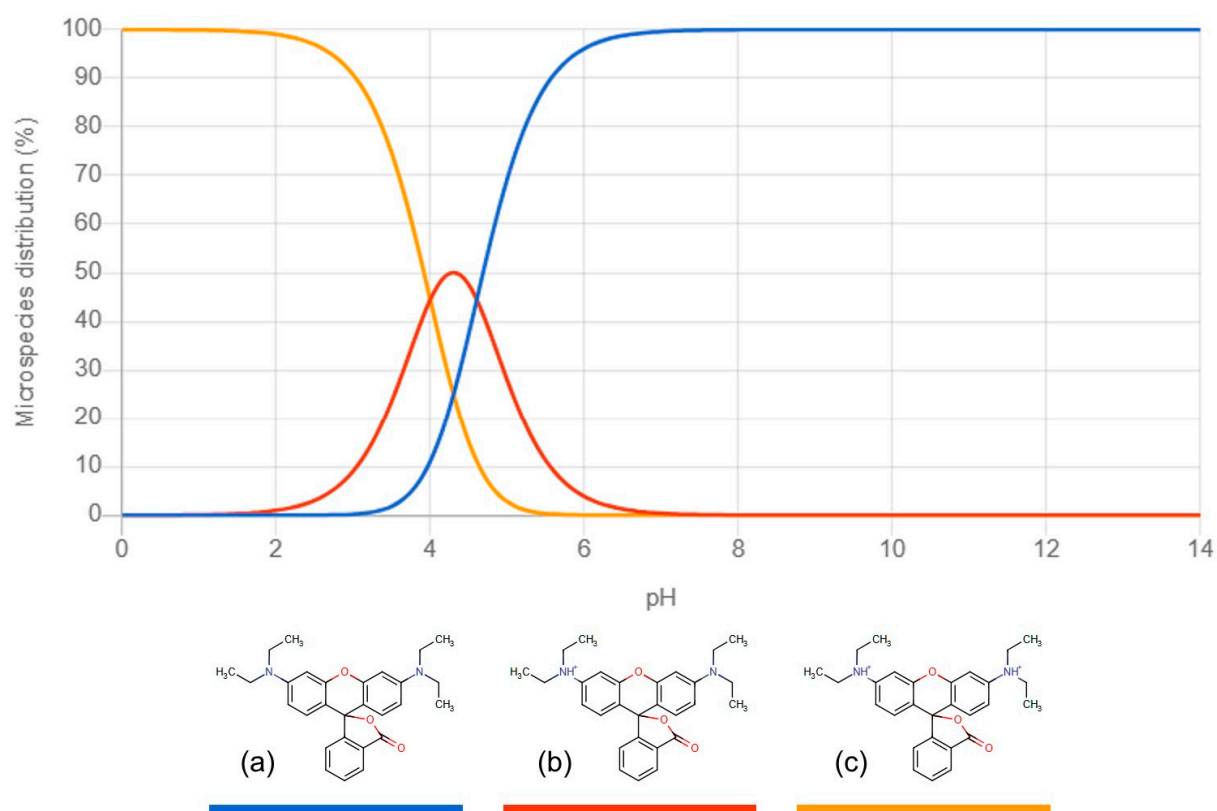
<sup>2</sup> Department of Chemistry, University of Nevada, Reno, 1664 N. Virginia Street, Reno, NV 89557-0216, USA; mmfizer@gmail.com

\* Correspondence: yaroslav.bazel@upjs.sk

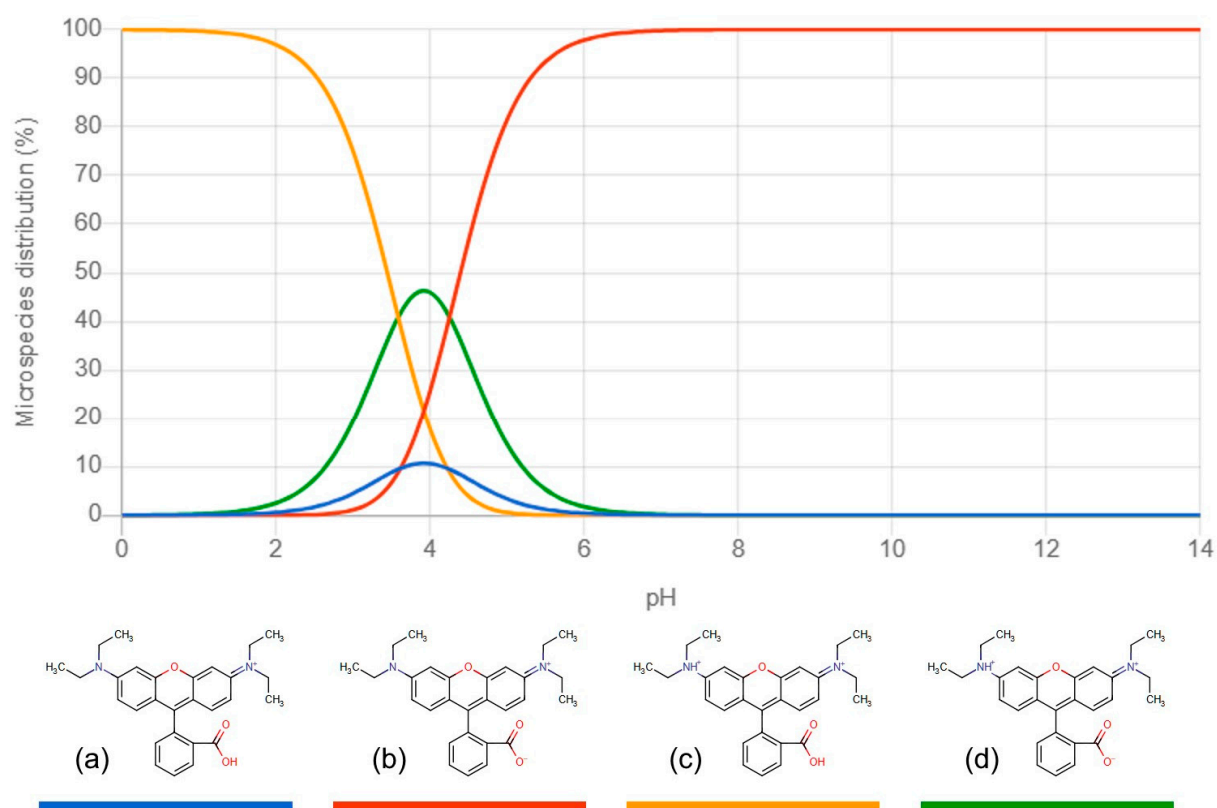
## Supplementary information

### CONTENT

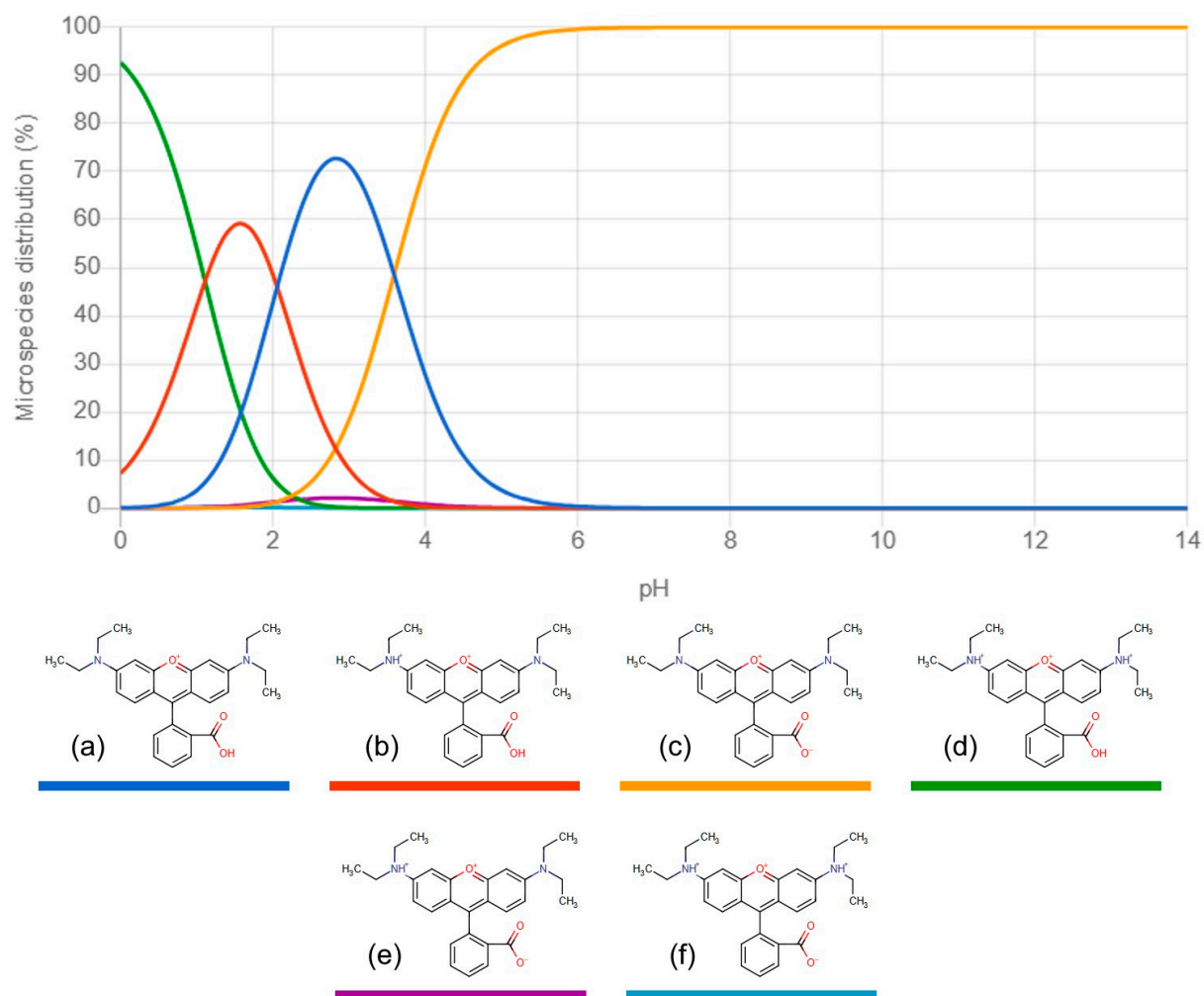
Item	Page
<b>Figure S1.</b> The distribution of microspecies of lactone (cyclic) forms of RhB at different pH. Calculated with Chemicalized.	2
<b>Figure S2.</b> The distribution of microspecies of non-cyclic forms of RhB with localization of a positive charge over the diethylamino group nitrogen atom at different pH. Calculated with Chemicalized.	3
<b>Figure S3.</b> The distribution of microspecies of non-cyclic forms of RhB with localization of a positive charge over the pyran ring oxygen atom at different pH. Calculated with Chemicalized.	4
<b>Figure S4.</b> Relative Gibbs free energies of solvated structures. Neutral zwitterionic forms (a) and the cyclic lactone form (b). Mono-cationic forms CA-A2 (c), CA-A1 (d), CL-N (g), CL-O (f). Di-cationic forms DN-A1 (g), DN-A2 (h), DO-A1 (i), DO-A2 (j), DZ-N (k), DZ-O (l).	5
<b>Figure S5.</b> FT-IR spectra of hexanol (a), TBAB (e), and DESs composed of TBAB and hexanol in molar ratios of 1:1 (b), 1:2 (c), and 1:3 (d): (A) full spectra; (B) zoomed region of 2700–3600 cm <sup>-1</sup> ; (C) zoomed region of 650–1600 cm <sup>-1</sup> .	6
<b>Table S1.</b> Assignment of specific vibrations to the selected peaks in the FTIR spectrum of hexanol.	7
<b>Table S2.</b> Assignment of specific vibrations to the selected peaks in the FTIR spectrum of DES with TBAB: hexanol ratio equals 1:1.	7
<b>Table S3.</b> Assignment of specific vibrations to the selected peaks in the FTIR spectrum of DES with TBAB: hexanol ratio equals 1:2.	8
<b>Table S4.</b> Assignment of specific vibrations to the selected peaks in the FTIR spectrum of DES with TBAB: hexanol ratio equals 1:3.	8
<b>Table S5.</b> Assignment of specific vibrations to the selected peaks in the FTIR spectrum of TBAB.	9



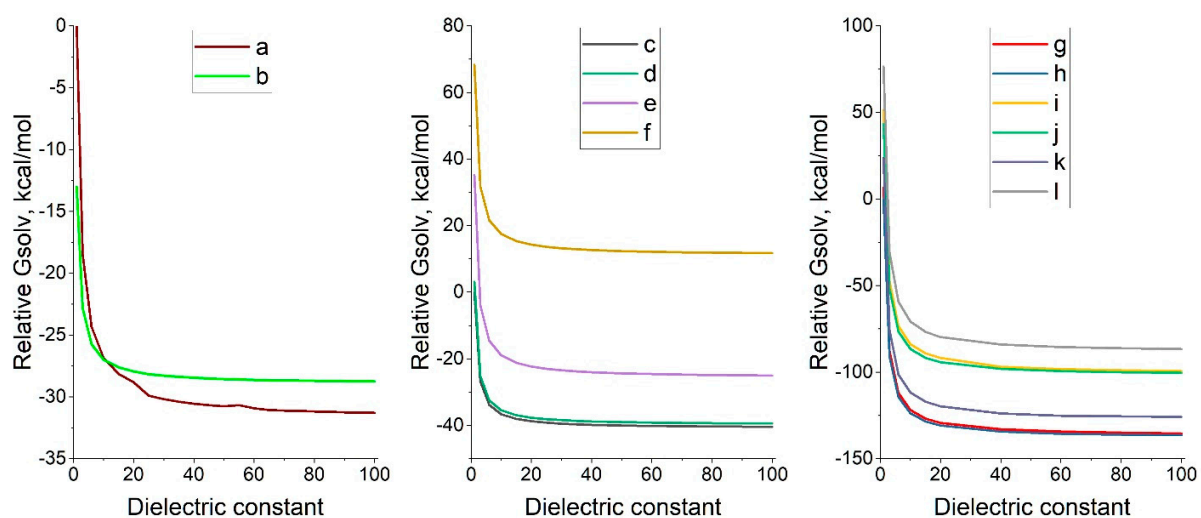
**Figure S1.** The distribution of microspecies of lactone (cyclic) forms of RhB at different pH. Calculated with Chemicalized.



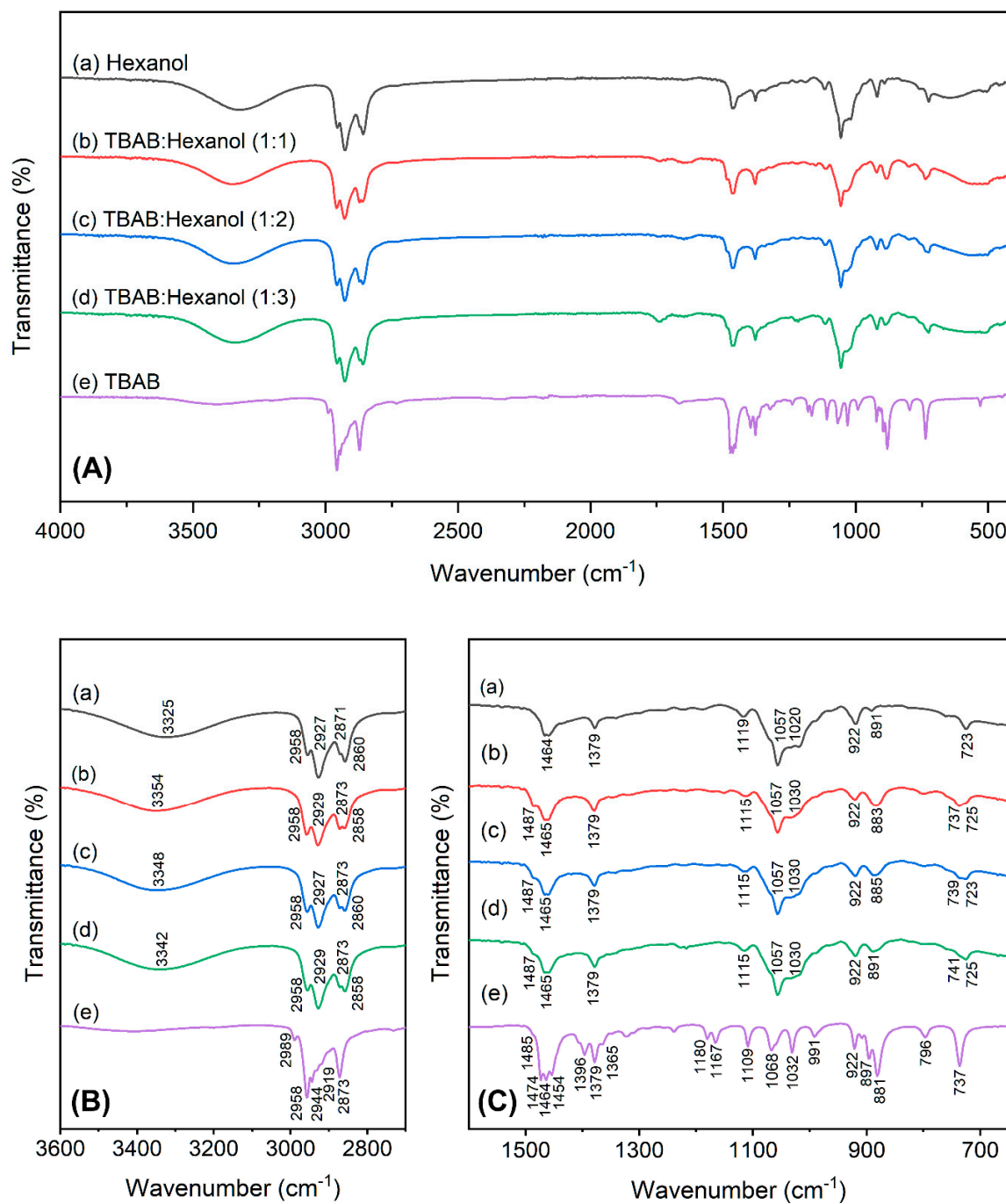
**Figure S2.** The distribution of microspheres of non-cyclic forms of RhB with localization of a positive charge over the diethylamino group nitrogen atom at different pH. Calculated with Chemicalized.



**Figure S3.** The distribution of microspecies of non-cyclic forms of RhB with localization of a positive charge over the pyran ring oxygen atom at different pH. Calculated with Chemicalized.



**Figure S4.** Relative Gibbs free energies of solvated structures. Neutral zwitterionic forms (a) and the cyclic lactone form (b). Mono-cationic forms CA-A2 (c), CA-A1 (d), CL-N (g), CL-O (f). Di-cationic forms DN-A1 (g), DN-A2 (h), DO-A1 (i), DO-A2 (j), DZ-N (k), DZ-O (l).



**Figure S5.** FT-IR spectra of hexanol (a), TBAB (e), and DESs composed of TBAB and hexanol in molar ratios of 1:1 (b), 1:2 (c), and 1:3 (d): (A) full spectra; (B) zoomed region of 2700–3600  $\text{cm}^{-1}$ ; (C) zoomed region of 650–1600  $\text{cm}^{-1}$ .

**Table S1.** Assignment of specific vibrations to the selected peaks in the FTIR spectrum of hexanol.\*

Wavenumber, cm <sup>-1</sup>	Predominant vibrations
3325	$\nu(\text{OH})$ , O–H stretching vibrations
2958	$\nu_{\text{as}}(\text{CH}_3)$ , antisymmetric C–H stretching of the methyl group
2927	$\nu_{\text{as}}(\text{CH}_2)$ , antisymmetric C–H stretching of methylene groups
2871	$\nu_{\text{s}}(\text{CH}_3)$ , symmetric C–H stretching of the methyl group
2860	$\nu_{\text{s}}(\text{CH}_2)$ , symmetric C–H stretching of methylene groups
1464	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$ , scissoring H–C–H bending of methylene groups and antisymmetric H–C–H bending of the methyl group
1379	$\omega(\text{CH}_2) + \omega(\text{CH}_3)$ , wagging H–C–H bending of methylene and methyl groups
1119	$\delta(\text{C–O–H})$ , bending of the $\text{H}_2\text{C–O–H}$ group
1057	$\nu(\text{C–OH})$ , C–O bond stretching vibration of the $\text{H}_2\text{C–OH}$ fragment
1020	$\nu(\text{CH}_2\text{–CH}_2)$ , C–C bond stretching vibrations
922	$\nu_{\text{s}}(\text{C–C–C})$ , symmetric C–C–C stretching of the carbon chain
891	$\nu_{\text{s}}(\text{C–C–CH}_3)$ , symmetric C–C–CH <sub>3</sub> stretching of the carbon chain
723	$\rho(\text{CH}_2)$ , rocking H–C–H bending of methylene groups

\*  $\nu_{\text{s}}$  – symmetric bond stretching vibration;  $\nu_{\text{as}}$  – antisymmetric bond stretching vibration;  $\delta$  – symmetric bond stretching vibration;  $\delta$  – scissoring bending vibration;  $\rho$  – rocking bending vibration;  $\omega$  – wagging bending vibration.

**Table S2.** Assignment of specific vibrations to the selected peaks in the FTIR spectrum of DES with TBAB: hexanol ratio equals 1:1.\*

Wavenumber, cm <sup>-1</sup>	Predominant vibrations
3354	$\nu(\text{OH})$ , O–H stretching vibrations
2958, 2929	$\nu_{\text{as}}(\text{CH}_2) + \nu_{\text{as}}(\text{CH}_3)$ , antisymmetric C–H stretching of methylene and methyl groups
2873, 2858	$\nu_{\text{s}}(\text{CH}_2) + \nu_{\text{s}}(\text{CH}_3)$ , symmetric C–H stretching of methylene and methyl groups
1487, 1465	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$ , scissoring H–C–H bending of methylene groups and antisymmetric H–C–H bending of the methyl group
1379	$\omega(\text{CH}_2) + \omega(\text{CH}_3)$ , wagging H–C–H bending of methylene and methyl groups
1115	$\delta(\text{C–O–H})$ , bending of the $\text{H}_2\text{C–O–H}$ group
1057	$\nu(\text{C–OH})$ , C–O bond stretching vibration of the $\text{H}_2\text{C–OH}$ fragment
1030	$\nu(\text{CH}_2\text{–CH}_2)$ , C–C bond stretching vibrations
922	$\nu_{\text{s}}(\text{C–C–C})$ , symmetric C–C–C stretching of the carbon chain
883	$\nu_{\text{s}}(\text{C–C–CH}_3)$ , symmetric C–C–CH <sub>3</sub> stretching of the carbon chain
737, 723	$\rho(\text{CH}_2)$ , rocking H–C–H bending of methylene groups

\*  $\nu_{\text{s}}$  – symmetric bond stretching vibration;  $\nu_{\text{as}}$  – antisymmetric bond stretching vibration;  $\delta$  – symmetric bond stretching vibration;  $\delta$  – scissoring bending vibration;  $\rho$  – rocking bending vibration;  $\omega$  – wagging bending vibration.

**Table S3.** Assignment of specific vibrations to the selected peaks in the FTIR spectrum of DES with TBAB: hexanol ratio equals 1:2.\*

Wavenumber, cm <sup>-1</sup>	Predominant vibrations
3348	$\nu(\text{OH})$ , O–H stretching vibrations
2958, 2927	$\nu_{\text{as}}(\text{CH}_2) + \nu_{\text{as}}(\text{CH}_3)$ , antisymmetric C–H stretching of methylene and methyl groups
2873, 2860	$\nu_{\text{s}}(\text{CH}_2) + \nu_{\text{s}}(\text{CH}_3)$ , symmetric C–H stretching of methylene and methyl groups
1487, 1465	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$ , scissoring H–C–H bending of methylene groups and antisymmetric H–C–H bending of the methyl group
1379	$\omega(\text{CH}_2) + \omega(\text{CH}_3)$ , wagging H–C–H bending of methylene and methyl groups
1115	$\delta(\text{C–O–H})$ , bending of the $\text{H}_2\text{C–O–H}$ group
1057	$\nu(\text{C–OH})$ , C–O bond stretching vibration of the $\text{H}_2\text{C–OH}$ fragment
1030	$\nu(\text{CH}_2\text{–CH}_2)$ , C–C bond stretching vibrations
922	$\nu_{\text{s}}(\text{C–C–C})$ , symmetric C–C–C stretching of the carbon chain
885	$\nu_{\text{s}}(\text{C–C–CH}_3)$ , symmetric C–C–CH <sub>3</sub> stretching of the carbon chain
739, 723	$\rho(\text{CH}_2)$ , rocking H–C–H bending of methylene groups

\*  $\nu_{\text{s}}$  – symmetric bond stretching vibration;  $\nu_{\text{as}}$  – antisymmetric bond stretching vibration;  $\delta$  – symmetric bond stretching vibration;  $\delta$  – scissoring bending vibration;  $\rho$  – rocking bending vibration;  $\omega$  – wagging bending vibration.

**Table S4.** Assignment of specific vibrations to the selected peaks in the FTIR spectrum of DES with TBAB: hexanol ratio equals 1:3.\*

Wavenumber, cm <sup>-1</sup>	Predominant vibrations
3342	$\nu(\text{OH})$ , O–H stretching vibrations
2958, 2929	$\nu_{\text{as}}(\text{CH}_2) + \nu_{\text{as}}(\text{CH}_3)$ , antisymmetric C–H stretching of methylene and methyl groups
2873, 2858	$\nu_{\text{s}}(\text{CH}_2) + \nu_{\text{s}}(\text{CH}_3)$ , symmetric C–H stretching of methylene and methyl groups
1487, 1465	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$ , scissoring H–C–H bending of methylene groups and antisymmetric H–C–H bending of the methyl group
1379	$\omega(\text{CH}_2) + \omega(\text{CH}_3)$ , wagging H–C–H bending of methylene and methyl groups
1115	$\delta(\text{C–O–H})$ , bending of the $\text{H}_2\text{C–O–H}$ group
1057	$\nu(\text{C–OH})$ , C–O bond stretching vibration of the $\text{H}_2\text{C–OH}$ fragment
1030	$\nu(\text{CH}_2\text{–CH}_2)$ , C–C bond stretching vibrations
922	$\nu_{\text{s}}(\text{C–C–C})$ , symmetric C–C–C stretching of the carbon chain
891	$\nu_{\text{s}}(\text{C–C–CH}_3)$ , symmetric C–C–CH <sub>3</sub> stretching of the carbon chain
741, 725	$\rho(\text{CH}_2)$ , rocking H–C–H bending of methylene groups

\*  $\nu_{\text{s}}$  – symmetric bond stretching vibration;  $\nu_{\text{as}}$  – antisymmetric bond stretching vibration;  $\delta$  – symmetric bond stretching vibration;  $\delta$  – scissoring bending vibration;  $\rho$  – rocking bending vibration;  $\omega$  – wagging bending vibration.



**Table S5.** Assignment of specific vibrations to the selected peaks in the FTIR spectrum of TBAB.\*

Wavenumber, cm <sup>-1</sup>	Predominant vibrations
2989, 2958 2944	$\nu_{\text{as}}(\text{CH}_2) + \nu_{\text{as}}(\text{CH}_3)$ , antisymmetric C–H stretching of methylene and methyl groups
2919, 2873	$\nu_{\text{s}}(\text{CH}_2) + \nu_{\text{s}}(\text{CH}_3)$ , symmetric C–H stretching of methylene and methyl groups
1454–1485	$\delta(\text{CH}_2) + \delta(\text{CH}_3)$ , scissoring H–C–H bending of methylene groups and antisymmetric H–C–H bending of the methyl group
1396, 1379, 1365	$\omega(\text{CH}_2) + \omega(\text{CH}_3) + \tau(\text{CH}_2) + \tau(\text{CH}_3)$ , wagging and twisting H–C–H bending of methylene and methyl groups
1180, 1167	$\delta(\text{CNC}) + \omega(\text{CNC})$ , scissoring and wagging C–N–C bending
1109, 1068, 1032, 991	$\nu(\text{CH}_2\text{--CH}_2) + \nu(\text{N--CH}_2)$ , C–C and N–C bonds stretching vibrations
922	$\nu_{\text{s}}(\text{C--C--C})$ , symmetric C–C stretching of the carbon chain
897	$\nu_{\text{s}}(\text{C--C--CH}_3)$ , symmetric C–CH <sub>3</sub> stretching of the carbon chain
881	$\nu_{\text{s}}(\text{N--C--C})$ , symmetric N–C–C stretching
796	$\nu(\text{N--CH}_2) + \tau(\text{N--CH}_2)$ , N–C bonds stretching and torsion C–N–C–C vibrations
737	$\rho(\text{CH}_2)$ , rocking H–C–H bending of methylene groups

\*  $\nu_{\text{s}}$  – symmetric bond stretching vibration;  $\nu_{\text{as}}$  – antisymmetric bond stretching vibration;  $\delta$  – symmetric bond stretching vibration;  $\delta$  – scissoring bending vibration;  $\rho$  – rocking bending vibration;  $\omega$  – wagging bending vibration;  $\tau$  – twisting bending vibration.