

Supporting Information

The path towards type V deep eutectic solvents: inductive effect and steric hindrance in the system tert-butanol + perfluoro tert-butanol

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- **Sample preparation**

Binary mixtures of different molar fraction of *tert*-butanol with perfluoro-*tert*-butanol [TBF + TBH] were prepared gravimetrically using an analytical balance, Mettler Toledo, model AG245, with a mass resolution of ± 0.01 mg. All mixtures were prepared and handle for the calorimetric measurements in a glove box (Captair pyramid 2200) under nitrogen atmosphere and kept in sealed glass bottles under nitrogen. The composition uncertainty was estimated as better than ± 0.01 mole fraction.

- **Solid-liquid phase diagram of [TBF + TBH]**

The following thermal procedure was done for the study of the solid-liquid equilibrium of the [TBF +TBH] binary mixtures: first an isothermal step of 1 min at 298 K, followed by a fast cooling (scanning rate $50 \text{ K}\cdot\text{min}^{-1}$) until $178 \text{ K}\cdot\text{min}^{-1}$ and it was done an isothermal step of 15 min to to insure complete crystallization; a heating step of $5 \text{ K}\cdot\text{min}^{-1}$ was performed until total isotropization. The eutectic temperatures, T_{eutectic} , solid-solid transition temperatures, T_{ss} , melting temperatures, T_{melting} , for the different compositions (molar fraction of TBF, x_{TBF}) of the binary mixtures TBF+ TBH are given in Table SI.1.

▪ Excess Enthalpies

The partial excess molar enthalpies of TBF in TBH, \bar{H}_2^E (TBH being defined as the component 1 and TBF component 2) at atmospheric pressure and at $T = 298.15 \pm 0.01$ K were experimentally obtained by Isothermal Titration Calorimetry (ITC). The calorimetric experiments consisted in subsequent injections of 10-40 μL of TBF to a sample of TBH or TBH-TBF binary solutions.

Each injection generated a heat flow signal, which was allowed to return to baseline before each new injection (see a typical experiment in figure SI.1). The area of the peak generated is proportional to the heat involved in the mixing experiment, which is directly related with the partial excess molar enthalpy as shown in the equation 1.

$$\bar{H}_2^E = \left(\frac{Q_i}{\delta m_2} \right)_{p,T,n_1} \quad \text{eq.1}$$

The experimental data, \bar{H}_2^E , summarized in table SI.1, was fitted using the derivative of the Redlich–Kister fit (The values of the partial excess molar enthalpies obtained from the fitting are also presented in table SI.1 and are represented in figure SI.2).

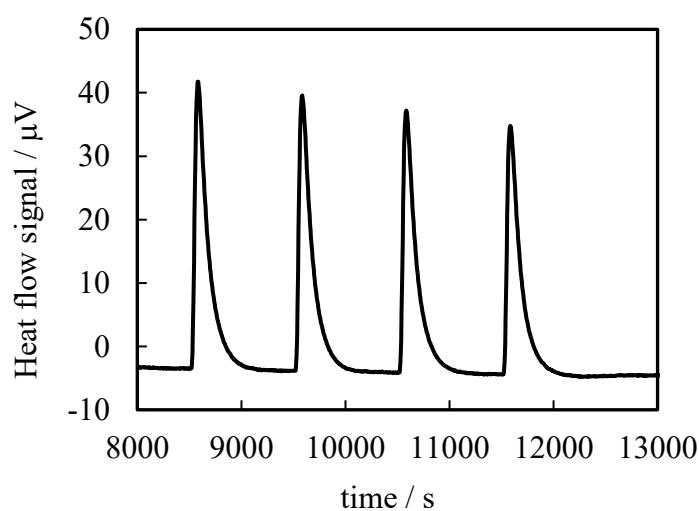


Figure SI.1. Plot of the typical results obtained from ITC for the injection of 12 μL of TBF in a solution of $x_2 = 0.8$ (initial concentration).

Table SI.1. Different compositions (molar fraction of TBF, x_{TBF}) of the binary mixtures TBF + TBH, eutectic temperatures, T_{eutectic} , solid-solid transition temperatures, T_{ss} , and melting temperatures, T_{m} .^a

x_{TBF}	$m_{\text{sample}}/\text{mg}$	$T_{\text{eutectic I}} / \text{K}$	$T_{\text{eutectic II}} / \text{K}$	$T_{\text{eutectic III}} / \text{K}$	T_{ss} / K	$T_{\text{melting}} / \text{K}$
0.062	13.83	241.6				280.7
0.103	14.30	240.2				277.7
0.108	15.22	243.2				273.0
0.156	18.18	242.0				259.3
0.196	12.18	241.0				251.8
0.200	17.93	242.0				249.2
0.206	18.42	242.0				249.4
0.207	11.35	241.3				247.1
0.248	13.63	242.2				245.0
0.248	15.26	241.6				244.5
0.251	10.45	242.1				247.1
0.300	15.40	242.7				248.9
0.331	9.70					250.3
0.380	13.86		231.1			243.3
0.394	14.73		232.5			246.1
0.399	6.03		233.2			244.9
0.454	25.53		234.1			238.7
0.506	26.16					235.7
0.596	5.11			222.9		232.6
0.597	15.68			223.1		229.8
0.695	15.78			221.4		226.7
0.738	9.44			221.1		223.8
0.748	44.92			223.7		226.2
0.797	17.30			225.2		228.9
0.842	8.18			225.6		231.0
0.850	8.64			221.7		232.7
0.901	26.67				226.2	239.7
0.951	13.18				235.2	246.3
0.953	27.93				235.4	247.2

^aThe uncertainty of the experimental results σ (temperature) was estimated as ± 1.0 K for the temperature.

Table SI.2. Experimental and fitted (Redlich–Kister equation, $n=4$) results of the partial excess molar enthalpy, \bar{H}_2^E .

x_{TBF}	\bar{H}_2^E <i>experimental data</i> (kJ·mol ⁻¹)	\bar{H}_2^E <i>fitted (fitted $n=4$)</i> (kJ·mol ⁻¹)
0.021	-20.240	-20.230
0.042	-19.968	-19.290
0.118	-16.916	-17.166
0.128	-16.920	-16.984
0.138	-16.727	-16.815
0.210	-15.049	-15.636
0.219	-15.020	-15.474
0.228	-14.819	-15.311
0.308	-13.202	-13.515
0.317	-13.096	-13.291
0.325	-12.951	-13.066
0.402	-11.823	-10.683
0.409	-11.707	-10.429
0.416	-11.531	-10.179
0.502	-8.264	-7.185
0.508	-7.878	-6.959
0.515	-7.426	-6.740
0.609	-3.297	-3.770
0.613	-3.230	-3.640
0.618	-3.104	-3.514
0.623	-3.016	-3.394
0.705	-1.504	-1.585
0.709	-1.460	-1.514
0.713	-1.406	-1.448
0.717	-1.351	-1.384
0.811	-0.383	-0.338
0.814	-0.364	-0.320
0.817	-0.352	-0.304
0.819	-0.329	-0.288
0.904	-0.026	-0.021
0.908	-0.016	-0.017
0.912	-0.010	-0.013
0.915	-0.010	-0.011
0.919	-0.009	-0.009

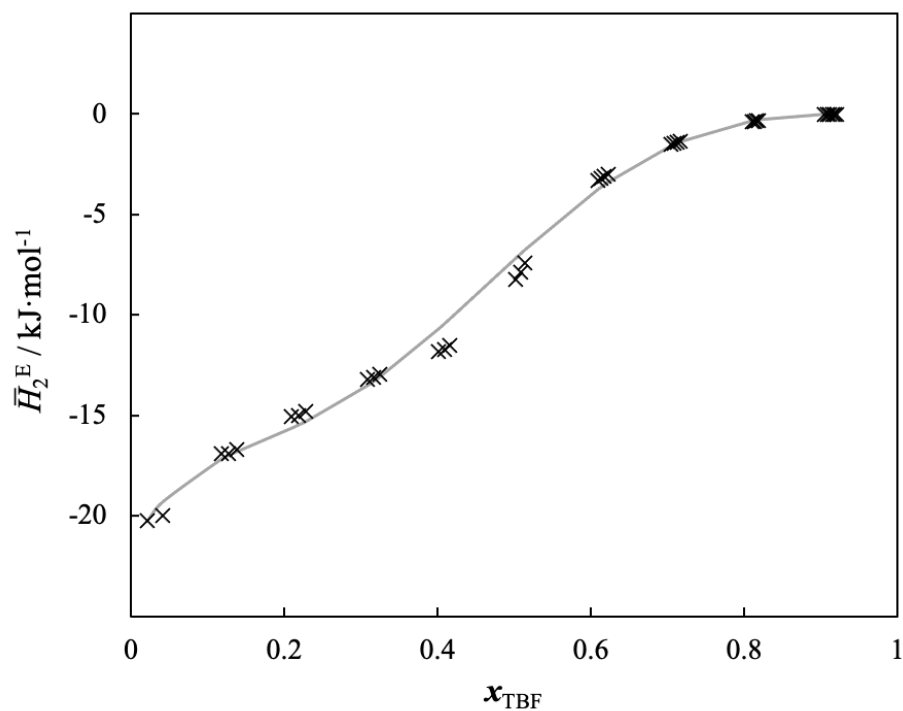


Figure SI.2. Partial excess molar enthalpy, \bar{H}_2^E (× experimental results and — results obtained by the Redlich–Kister fit, $n = 4$) versus molar fraction of TBF, x_{TBF} .

Table SI.3. Derivative Redlich–Kister equation coefficients A_i ($n = 4$). Binary mixtures : TBH (x_1) +TBF (x_2) .

A_i	Values / $\text{kJ}\cdot\text{mol}^{-1}$
A0	-25.8873
A1	3.0927
A2	8.9913
A3	-3.8657
A4	-3.8094

Table SI.4. Excess molar enthalpy of mixing, H^E derivative from the Redlich–Kister equation and from the parameters A_i ($n=4$).

x_{TBF}	$H^E / \text{kJ}\cdot\text{mol}^{-1}$	$H_2^E / \text{kJ}\cdot\text{mol}^{-1}$	$H_1^E / \text{kJ}\cdot\text{mol}^{-1}$
0.00	0.000	-21.48	0.00
0.05	-1.004	-18.97	-0.06
0.10	-1.908	-17.54	-0.17
0.15	-2.749	-16.61	-0.30
0.20	-3.540	-15.80	-0.47
0.25	-4.278	-14.88	-0.74
0.30	-4.947	-13.73	-1.18
0.35	-5.525	-12.34	-1.86
0.40	-5.987	-10.74	-2.82
0.45	-6.309	-9.01	-4.10
0.51	-6.484	-7.28	-5.66
0.55	-6.461	-6.90	-6.05
0.60	-6.269	-5.55	-7.57
0.65	-5.900	-4.02	-9.65
0.70	-5.363	-2.71	-11.82
0.75	-4.676	-1.67	-13.98
0.80	-3.866	-0.91	-15.97
0.85	-2.962	-0.42	-17.66
0.90	-1.997	-0.14	-18.94
0.95	-1.001	-0.03	-19.74
1.00	0.000	0.00	-20.04

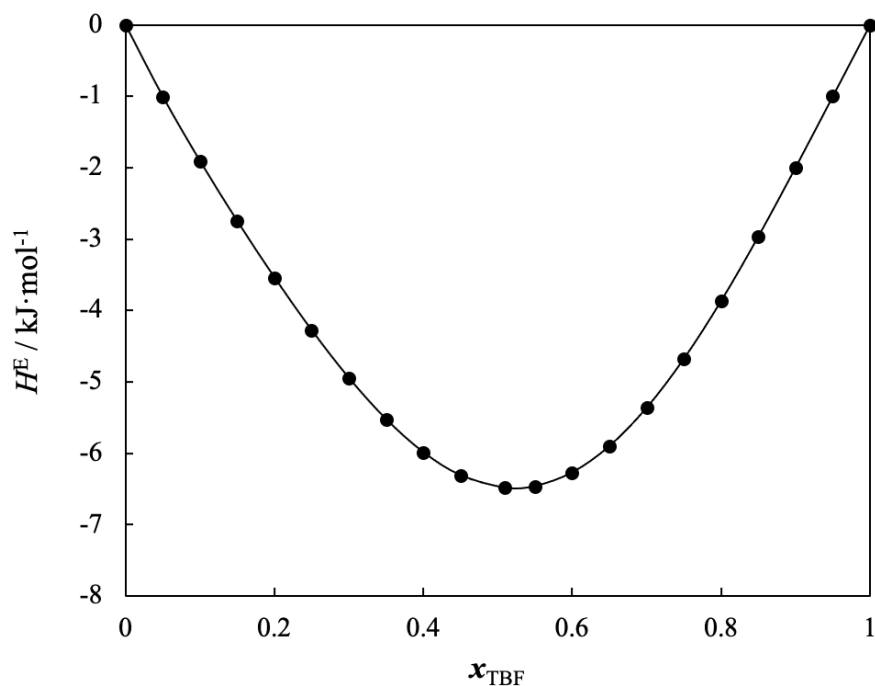


Figure SI.3. Excess molar enthalpy of mixing, H^E derivative from the Redlich–Kister equation and from the parameters A_i ($n = 4$).

Due to experimental difficulties, it was not possible to measure experimentally the partial excess molar enthalpy of TBH. Therefore, the fitting parameters obtained before were used to estimate the \bar{H}_1^E , as well as, the excess molar enthalpies of mixing. Using the experimental values of \bar{H}_2^E and the estimated \bar{H}_1^E values, it was calculated the “experimental” results of excess enthalpy of mixing. In figure SI.3 is represented the excess molar enthalpies of mixing obtained directly from the fitting parameters and from the experimental results. This figure acts as an indication of the uncertainty existent in the central area of the diagram, which is due to both lower absolute values of the \bar{H}_2^E and having only experimental values of one of the components.

Table SI.5. Experimental excess molar enthalpy of mixing, H^E derived by combing the experimental data set of H_2^E with the Redlich–Kister equation ($n= 4$).

x_{TBF}	$H_2^E / \text{kJ}\cdot\text{mol}^{-1}$ (experimental)	$H_1^E / \text{kJ}\cdot\text{mol}^{-1}$ (derived from RK fitting)	$H^E / \text{kJ}\cdot\text{mol}^{-1}$ (derived from experimental)
0.021	-20.24	-0.01	-0.444
0.042	-19.97	-0.04	-0.874
0.118	-16.92	-0.22	-2.189
0.128	-16.92	-0.24	-2.377
0.138	-16.73	-0.27	-2.533
0.210	-15.05	-0.52	-3.565
0.219	-15.02	-0.56	-3.727
0.228	-14.82	-0.61	-3.847
0.308	-13.20	-1.28	-4.956
0.317	-13.10	-1.38	-5.091
0.325	-12.95	-1.49	-5.212
0.402	-11.82	-2.86	-6.458
0.409	-11.71	-3.03	-6.580
0.416	-11.53	-3.21	-6.672
0.502	-8.26	-5.76	-7.016
0.508	-7.88	-5.99	-6.950
0.515	-7.43	-6.22	-6.840
0.609	-3.30	-10.02	-5.929
0.613	-3.23	-10.23	-5.936
0.618	-3.10	-10.43	-5.902
0.623	-3.02	-10.63	-5.888
0.705	-1.50	-14.18	-5.245
0.709	-1.46	-14.35	-5.211
0.713	-1.41	-14.51	-5.169
0.717	-1.35	-14.67	-5.123
0.811	-0.38	-17.99	-3.706
0.814	-0.36	-18.07	-3.656
0.817	-0.35	-18.14	-3.612
0.819	-0.33	-18.21	-3.559
0.904	-0.03	-19.78	-1.920
0.908	-0.02	-19.82	-1.835
0.912	-0.01	-19.86	-1.759
0.915	-0.01	-19.88	-1.692
0.919	-0.01	-19.91	-1.631
0.921	-0.01	-19.93	-1.574

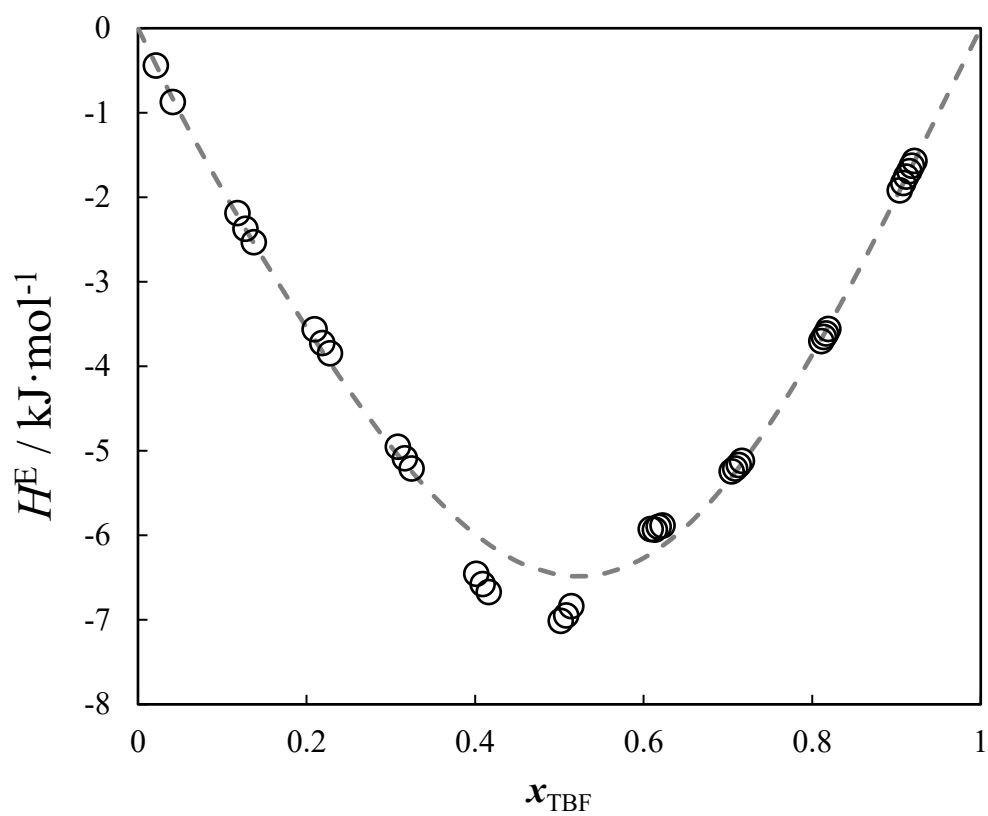


Figure SI.4. Derived experimental results of excess enthalpies of mixing, H^E , of TBF + TBH at 298.15 K (o) and Redlich–Kister fitting (---).

Table SI.6. Experimental densities and excess volumes for the TBH+TBF system at 298.15K as a function of composition.

$x(\text{TBF})$	$V^E / \text{g}\cdot\text{cm}^{-3}$
0 ($\rho = 0.78064 \text{ g}\cdot\text{cm}^{-3}$)	-
0.1019	0.14
0.1155	0.17
0.1325	0.18
0.1428	0.19
0.1868	0.33
0.2568	0.41
0.2880	0.51
0.3267	0.52
0.3388	0.52
0.3788	0.55
0.3991	0.50
0.4283	0.49
0.4495	0.49
0.4918	0.35
0.5041	0.31
0.6240	0.10
0.6326	0.10
0.6449	0.06
0.7098	-0.03
0.7115	0.03
0.7197	-0.01
0.7991	-0.01
0.8552	-0.04
0.8889	-0.03
0.8921	0.00
1 ($\rho = 1.68145 \text{ g}\cdot\text{cm}^{-3}$)	-