SUPPLEMENTARY INFORMATION

Examining the Potential of Type V DES for Metal Solvent Extraction

Nicolas Schaeffer,[a*] Inês Vaz,[a] Maísa Saldanha Pinheiro,[a] Felipe Olea,[b] Takafumi Hanada,[c] Sandrine Dourdain,[d] João A.P. Coutinho[a]

[a] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

[b] Laboratory of Separation Process Intensification (SPI), Department of Chemical Engineering and Bioprocess, University of Santiago de Chile (USACH)

[c] Department of Applied Chemistry, Graduate School of Technology, Industrial and Social Sciences, Tokushima University, 2-1 Minamijosanjima, Tokushima, Japan

[d] Institut de Chimie Séparative de Marcoule, ICSM, CEA, CNRS, ENSCM, Univ Montpellier, BP 17171, Marcoule, 30207, Bagnols-sur-Cèze, France

* Corresponding email: nicolas.schaeffer@ua.pt

Table S1. Experimental solid-liquid equilibrium data (mole fraction of thymol, $x_{Thymol,}$ and melting temperature, T) measured in this work at atmospheric pressure for binary mixtures of thymol with benzo-12-crown-4 ether. The melting properties (melting temperature, T_m and enthalpy of fusion, ΔH_m) of benzo-12-crown-4 ether were measured by differential scanning calorimetry as T_m = 319.21 K and ΔH_m = 32.41 kJ mol^{-1}.

x_{Thymol}	T
0.000	319.21
0.137	313.57
0.220	307.96
0.301	297.56
0.409	266.80
0.501	-
0.600	-
0.685	-
0.785	304.47
0.898	318.13
1.000	323.50

Table S2. The activity coefficients at infinite dilution of the HBA ($\ln\gamma_{HBA}$) in HBA-HBD eutectic mixtures at $x_{HBA} = 0.5$. The labelling of HBDs and HBAs correspond to those in **Figure 3** of the manuscript.

		Hydrogen bond acceptors (HBA)								
		1'	**2'**	**3'**	**4'**	**5'**	**6'**	**7'**	**8'**	**9'**
Hydrogen Bond Donors (HBD)	**1**	0.499	0.445	0.543	0.318	0.567	0.539	0.221	0.307	0.669
	2	1.033	1.089	1.049	0.621	0.948	0.970	0.899	0.955	1.224
	3	1.047	1.084	1.037	0.668	0.975	0.970	0.968	0.975	1.194
	4	0.693	0.800	0.818	0.333	0.666	0.718	0.385	0.700	1.112
	5	1.420	1.321	1.688	0.619	1.264	1.598	1.073	1.755	1.718
	6	0.987	0.953	0.983	0.367	0.908	0.863	0.657	0.736	1.294
	7	0.797	0.851	0.871	0.307	0.723	0.739	0.457	0.651	1.186
	8	0.859	0.745	0.788	0.600	0.936	0.773	0.796	0.884	0.902
	9	0.408	0.317	0.418	0.258	0.527	0.421	0.123	0.159	0.527
	10	0.594	0.602	0.618	0.179	0.589	0.550	0.400	0.561	0.895
	11	0.756	0.771	0.793	0.395	0.757	0.729	0.564	0.737	1.014
	12	0.844	0.852	0.911	0.343	0.763	0.849	0.742	1.307	1.119

Table S3. List of $\Delta_m H_i$, $\Delta_m S_i$, *and* $T_{m,i}$ for reported components in Type V "deep" and ideal eutectic solvents.

Compound	$\Delta_m H$ (kJ.mol^{-1})	$\Delta_m S$ (J.mol^{-1}K-1)	T_m (K)	Ref
1,10-phenanthroline	15.50	39.57	391.7	[1]
Pyridine	8.28	35.77	231.5	[2]
2,2'-bipyridine	20.40	59.13	345.00	[3]
Lidocaine	16.40	48.14	340.7	[4]
Phenol	11.50	36.61	314.1	[5]
2,6-Di-tert-butyl-4-methylphenol	19.85	58.09	341.7	[6]
Thymol	19.65	60.74	323.5	[7]
Eugenol	18.72	69.54	269.2	[8]
Camphor	6.30	13.92	452.7	[9]
Menthol	12.89	40.83	315.7	[7]
Borneol	7.30	15.16	481.6	[9]
Acetylsalicylic Acid	23.01	56.48	407.4	[10]
trans-Ferulic Acid	30.50	68.55	444.9	[10]
Hydrocinnamic Acid	16.30	50.65	321.8	[11]
Salicylic Acid	24.45	56.72	431.1	[10]
Syringic Acid	33.70	70.16	480.3	[10]
Trioctylphosphine oxide	58.02	178.03	325.9	[11]
Triphenylphosphine oxide	24.22	56.08	431.9	[12]
N,N′-dihexylthiourea	20	62.75	318.7	[13]
Thenoyltrifluoroacetone	12.05	37.89	318.0	[14]
Benzoyltrifluoroacetone	19.17	61.25	313.0	[14]
18-Crown-6-ether	40.0	128.08	312.3	[15]
Dibenzo-18-Crown-6-ether	56.0	128.53	435.7	[15]
Dibenzo-24-Crown-8-ether	53.7	143.62	373.9	[15]
Dibenzo-30-Crown-10-ether	86.5	229.08	377.6	[15]
Malonic Acid	23.1	56.69	407.5	[16]
Levulinic Acid	9.22	30.11	306.2	[17]
Capric Acid	27.50	90.22	304.8	[7]
Decanol	33.7	120.36	280	[18]
Tertbutanol	5.6	18.75	298.7	[19]
perfluoro tert-butanol	8.2	32.58	251.7	[19]

Table S4. Reported viscosity and density of non-ionic hydrophobic eutectic solvents at 298 K as a function of composition and constituents (HTTA – thenoyltrifluoroacetone; HBTA – benzoyl trifluoroacetone; TOPO – trioctylphosphine oxide; TBP – tributylphosphate; D2EHPA – di(2-ethylhexyl)phosphoric acid).

System (Component 1 / Component 2)	$x_{Component1}$	Viscosity	Density	Ref
HBTA / N, N-bis (2-ethylhexyl) acetamide	0.50	16.82	0.976	[20]
HBTA / TBP	0.50	9.76	1.07	[20]
HBTA / TOPO	0.50	11.2	0.984	[20]
HTTA / TBP	0.50	5.04	1.13	[21]
HTTA / N, N-dimethylbenzamide	0.50	8.13	1.25	[21]
HTTA / TOPO	0.67	23.15	1.1	[21]
HBTA / TOPO	0.67	14.44	1.06	[21]
HTTA / TOPO	0.67	28.1	1.1	[14]
HBTA / TOPO	0.67	13.2	1.05	[14]
HTTA / Triphenyl phosphate	0.67	11.6	1.32	[14]
HTTA / DDA	0.67	18.06	1.06	[22]
HTTA / DDA	0.50	16.24	1.05	[22]
HTTA / DDA	0.33	12.85	0.97	[22]
TOPO / Decanol	0.33	30.3	0.85	[23]
TOPO / Thymol	0.50	69.93	0.898	[11]
TOPO / Decanoic acid	0.50	44.11	0.881	[11]
TOPO / Phenol	0.33	12.38	0.933	[24]
TOPO / Phenol	0.50	43.0	0.907	[24]
TOPO / Dodecanol	0.33	27.52	0.849	[25]
TOPO / Dodecanol	0.25	25.77	0.846	[25]
TOPO / Dodecanol	0.20	23.55	0.843	[25]
TOPO / Dodecanol	0.17	23.53	0.842	[25]
TOPO / Dodecanol	0.14	21.19	0.841	[25]
TOPO / Malonic acid	0.55	-	0.941	[26]
TOPO / Levulinic acid	0.40	-	0.940	[26]
Hydrocinamic acid / Decanoic acid	0.50	11.29	0.978	[11]
Decanoic acid / Dodecanoic acid/	0.67	10.76	0.894	[27]

Decanoic acid / Lidocaine	0.67	237.5	0.958	[28]
Decanoic acid / Thymol	0.50	12.16	0.930	[7]
Decanoic acid / Menthol	0.40	18.85	0.897	[7]
Thymol / Phenanthroline	0.80	75.31	1.024	[29]
Thymol / 2-methyl-2,4-pentanediol	0.67	32.69	0.959	[30]
Menthol / 2-methyl-2,4-pentanediol	0.67	68.39	0.901	[30]
Thymol / Menthol	0.50	53.14	0.937	[8]
Menthol / Camphor	0.50	16.42	0.924	[8]
Menthol / Borneol	0.70	110.4	0.915	[8]
Thymol / Camphor	0.50	20.8	0.967	[8]
Menthol / D2EHPA	0.50	31.28	0.947	[31]
N,N-diisooctylacetamide / Decanol	0.50	27.05	0.866	[32]

Table S5. Experimentally reported Kamlet-Taft parameters of non-ionic eutectic solvents.

Component 1	Component 2	$x_{Component1}$	α	β	π	Ref
Menthol	Acetic acid	0.50	1.64	0.6	0.53	[33]
	Levulinic acid	0.50	1.56	0.58	0.66	
	Octanoic acid	0.50	1.77	0.5	0.41	
	Dodecanoic acid	0.33	1.79	0.57	0.37	
Menthol	Octanoic acid	0.43	0.85	0.43	0.39	[7]
	Decanoic acid	0.57	0.84	0.45	0.35	
	Dodecanoic acid	0.68	0.79	0.54	0.37	
	Tetradecanoic acid	0.78	0.75	0.5	0.38	
	Hexadecanoic acid	0.85	0.71	0.57	0.38	
	Octadecanoic acid	0.91	0.68	0.64	0.38	
Thymol	Octanoic acid	0.29	1.1	0.05	0.67	
	Decanoic acid	0.43	1.11	0.05	0.71	
	Dodecanoic acid	0.55	1.05	0.02	0.75	
	Tetradecanoic acid	0.67	1.13	0.02	0.84	
	Hexadecanoic acid	0.76	1.11	0.01	0.87	
	Octadecanoic acid	0.84	1.1	0.05	0.94	
Menthol	Thymol	0.10	1	0.15	0.97	[8]
		0.20	0.97	0.18	0.9	
		0.30	0.92	0.22	0.84	
		0.40	0.88	0.23	0.83	
		0.50	0.84	0.28	0.77	
		0.60	0.79	0.32	0.72	
		0.70	0.7	0.36	0.67	
		0.80	0.64	0.48	0.59	
		0.90	0.56	0.53	0.53	
Menthol	Camphor	0.50	0.41	0.61	0.52	
	Borneol	0.70	0.53	0.63	0.43	
	Sobrerol	0.95	0.52	0.68	0.43	
Thymol	Camphor	0.30	0.68	0.45	0.59	
	Camphor	0.40	0.71	0.41	0.62	

	Camphor	0.50	0.82	0.34	0.69
	Camphor	0.60	0.88	0.26	0.77
	Camphor	0.70	0.94	0.23	0.85
	Camphor	0.80	0.97	0.18	0.93
	Camphor	0.90	1.01	0.17	0.98
	Borneol	0.50	0.87	0.27	0.78
	Sobrerol	0.70	0.99	0.11	0.94

REFERENCES

1. Chirico, R. D., Kazakov, A. F. & Steele, W. V. Thermodynamic properties of three-ring aza-aromatics. 2. Experimental results for 1,10-phenanthroline, phenanthridine, and 7,8-benzoquinoline, and mutual validation of experiments and computational methods. *J Chem Thermodyn* **42**, 581–590 (2010).

2. Domalski, E. S. & Hearing, E. D. Heat Capacities and Entropies of Organic Compounds in the Condensed Phase. Volume III. *J Phys Chem Ref Data* **25**, 1 (2009).

3. Lipkind, D., Hanshaw, W. & Chickos, J. S. Hypothetical thermodynamic properties. Subcooled vaporization enthalpies and vapor pressures of polyaromatic heterocycles and related compounds. *J Chem Eng Data* **54**, 2930–2943 (2009).

4. Lazerges, M., Rietveld, I. B., Corvis, Y., Céolin, R. & Espeau, P. Thermodynamic studies of mixtures for topical anesthesia: Lidocaine–salol binary phase diagram. *Thermochim Acta* **497**, 124–128 (2010).

5. Andon, R. J. L., Counsell, J. F., Herington, E. F. G. & Martin, J. F. Thermodynamic properties of organic oxygen compounds. Part 7.—Calorimetric study of phenol from 12 to 330°K. *Trans Faraday Soc* **59**, 830–835 (1963).

6. Verevkin, S. P. Thermochemistry of phenols: buttress effects in sterically hindered phenols. *J Chem Thermodyn* **31**, 1397–1416 (1999).

7. Martins, M. A. R. *et al.* Tunable Hydrophobic Eutectic Solvents Based on Terpenes and Monocarboxylic Acids. *ACS Sustain Chem Eng* **6**, 8836–8846 (2018).

8. Martins, M. A. R. *et al.* Greener Terpene-Terpene Eutectic Mixtures as Hydrophobic Solvents. *ACS Sustain Chem Eng* **7**, 17414–17423 (2019).

9. Chandra, G. & Murthy, S. S. N. Dielectric and thermodynamic study of camphor and borneol enantiomers and their binary systems. *Thermochim Acta* **666**, 241–252 (2018).

10. Su, C. S. & Chen, Y. P. Correlation for the solubilities of pharmaceutical compounds in supercritical carbon dioxide. *Fluid Phase Equilib* **254**, 167–173 (2007).

11. Schaeffer, N. *et al.* Non-ionic hydrophobic eutectics-versatile solvents for tailored metal separation and valorisation. *Green Chem* **22**, 2810–2820 (2020).

12. Hulnink, J., van Miltenburg, K., Oonk, H. A. J., Schuljff, A. & Groen, P. Thermodynamic Functions and Vapor Pressures of Triphenylphosphine Oxide and 1,4-Bis(diphenylphosphino)butane Near the Melting Point. *J Chem Eng Data* **34**, 99–100 (1989).

13. van den Bruinhorst, A. *et al.* Hydrophobic eutectic mixtures as volatile fatty acid extractants. *Sep Purif Technol* **216**, 147–157 (2019).

14. Hanada, T. & Goto, M. Synergistic Deep Eutectic Solvents for Lithium Extraction. *ACS Sustain Chem Eng* **9**, 2152–2160 (2021).

15. Sánchez-Bulás, T., Cruz-Vásquez, O., Hernández-Obregón, J. & Rojas, A. Enthalpies of fusion, vaporisation and sublimation of crown ethers determined by thermogravimetry and differential scanning calorimetry. *Thermochim Acta* **650**, 123–133 (2017).

16. Hansen, A. R. & Beyer, K. D. Experimentally Determined Thermochemical Properties of the Malonic Acid/Water System: Implications for Atmospheric Aerosols. *J Phys Chem A* **108**, 3457–3466 (2004).

17. Acree, W. E. Thermodynamic properties of organic compounds: enthalpy of fusion and melting point temperature compilation. *Thermochim Acta* **189**, 37–56 (1991).

18. Van Miltenburg, J. C., Gabrielová, H. & Růžička, K. Heat capacities and derived thermodynamic functions of 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol between 5 K and 390 K. *J Chem Eng Data* **48**, 1323–1331 (2003).

19. Vaz, I. C. M. *et al.* The path towards type V deep eutectic solvents: inductive effects and steric hindrance in the system tert-butanol + perfluoro tert-butanol. *Phys Chem Chem Phys* **25**, 11227–11236 (2023).

20. Zhang, L., Li, J., Ji, L. & Li, L. Separation of lithium from alkaline solutions with hydrophobic deep eutectic solvents based on β-diketone. *J Mol Liq* **344**, 117729 (2021).

21. Luo, H. *et al.* Selective recovery of lithium from mother liquor of Li2CO3 by synergistic hydrophobic deep eutectic solvents: Performance and mechanistic insight. *Sep Purif Technol* **313**, 123353 (2023).

22. Chen, J. *et al.* A novel ternary hydrophobic deep eutectic solvent over a wide pH range for lithium recovery. *J Hazard Mater* **480**, 136398 (2024).

23. Yu, G. *et al.* Recovery of rare earth metal oxides from NdFeB magnet leachate by hydrophobic deep eutectic solvent extraction, oxalate stripping and calcination. *Hydrometallurgy* **223**, 106209 (2024).

24. Gilmore, M. *et al.* Hydrophobic Deep Eutectic Solvents Incorporating Trioctylphosphine Oxide: Advanced Liquid Extractants. *ACS Sustain Chem Eng* **6**, 17323–17332 (2018).

25. Ni, S. *et al.* A cleaner strategy for comprehensive recovery of waste SmCo magnets based on deep eutectic solvents. *Chem Eng J* **412**, 128602 (2021).

26. Byrne, E. L. *et al.* Hydrophobic functional liquids based on trioctylphosphine oxide (TOPO) and carboxylic acids. *Phys Chem Chem Phys* **22**, 24744–24763 (2020).

27. Florindo, C., Romero, L., Rintoul, I., Branco, L. C. & Marrucho, I. M. From Phase Change Materials to Green Solvents: Hydrophobic Low Viscous Fatty Acid−Based Deep Eutectic Solvents. A*CS Sustain Chem. Eng.* **6**, 3888–3895 (2018).

28. Bica, K., Shamshina, J., Hough, W. L., Macfarlane, D. R. & Rogers, R. D. Liquid forms of pharmaceutical co-crystals: exploring the boundaries of salt formation. *Chem Comm* **47**, 2267 (2011).

29. Crema, A. P. S. *et al.* New family of Type V eutectic solvents based on 1,10-phenanthroline and their application in metal extraction. *Hydrometallurgy* **215**, 105971 (2023).

30. Almustafa, G. *et al.* Boron extraction from aqueous medium using novel hydrophobic deep eutectic solvents. *Chem Eng J* **395**, 125173 (2020).

31. Zinov'eva, I. V., Kozhevnikova, A. V., Milevskii, N. A., Zakhodyaeva, Y. A. & Voshkin, A. A. Extraction of Cu(II), Ni(II), and Al(III) with the Deep Eutectic Solvent D2EHPA/Menthol. *Theor Found Chem Eng* **56**, 221–229 (2022).

32. Zhu, K., Wei, Q., Li, H. & Ren, X. Recovery of Titanium from Ilmenite HCl Leachate Using a Hydrophobic Deep Eutectic Solvent. *ACS Sustain Chem Eng* **10**, 2125–2135 (2022).

33. Florindo, C., McIntosh, A. J. S., Welton, T., Branco, L. C. & Marrucho, I. M. A closer look into deep eutectic solvents: exploring intermolecular interactions using solvatochromic probes. *Phys Chem Chem Phys* **20**, 206–213 (2017).