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Supporting information

Quantification of the liquid window of deep eutectic solvents

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1. Experimental materials and methods

Characterization of the individual components

The used chemicals were dried overnight under vacuum. The water content of the individual components was measured using a Metrohm 831 KF coulometer with a generator electrode with diaphragm and an 832 KF Thermoprep. Hydranal Coulomat AG was used as titration medium. The detection limit is 10 µg. Samples, with a mass of typically 1.5 g, were heated until fully melted in order to measure all the water present. Density measurements were carried out using a Microkinetics AccuPyc II 1340 helium pycnometer. Melting points and enthalpies of fusion were measured using a TA Q2000 Dynamic Scanning Calorimeter (DSC), the resulting thermograms can be found in Figure SI 2, Figure SI 3 and Figure SI 4 with the details of the measurements.

DES preparation and characterization

Glass containers, spatulas, and tweezers were dried overnight in an oven at 105 °C. The dried utensils were transferred into a glovebox with inert nitrogen atmosphere with typical

values of 0.5 ppm O_2 and 1.5 ppm H_2O. The overpressure in the glovebox was kept at 1.5-2.5 mbar. The mass of the individual components of the DES was determined using weighing boats and an analytical balance, inside the glovebox. The components were added together with a magnetic stirring bar in a glass vial. The mixture was then heated above the highest melting point (T_m) of the individual components while stirring, poured in a mortar, cooled down, and after crystallization ground with a pestle to obtain homogenous, fine powders. The samples were prepared over a wide composition range.

To measure the melting point of the DES mixtures a capillary melting point apparatus was used (Büchi melting point B-540). For this, two capillaries of each composition were prepared. Capillaries were filled with approximately 5.0 mm of fine sample powders and hermetically closed with hot glue. The samples were heated at a rate of 5 $K \cdot min^{-1}$ until the first liquid appeared, and the temperature was recorded. After cooling and crystallization for at least 24h, the process was repeated two more times at 1 $K \cdot min^{-1}$, until a uniform liquid was obtained. The eutectic temperature (solidus) was recorded upon the first appearance of some liquid during the first and second heating cycle. The melting point (liquidus) was recorded upon the disappearance of the last solids during the second and third heating cycle. For a given composition this was executed for at least two samples. During all heating cycles, images of the mixtures have been recorded using a Canon (EOS 50D, Macro Lens EF 100 mm 1:2.8 USM) photo camera, capturing a photo every 5 s.

The composition of the mixture in each capillary was determined by 1H-NMR spectroscopy (Brucker BZH 400/52) after the measurements. D2O (Cambridge Isotope Laboratories Inc. Deuterium oxide 99.9%, DLM-4-100, CAS 7789-20-0) was used as solvent. Figure SI 1 top panel shows a typical NMR spectrum of a mixture of erythritol with tetrapentylammonium bromide with the peaks assigned and integrated. The bottom panel of Figure SI 1 shows a typical NMR spectrum of succinic acid with tetrapentylammonium bromide, again the relevant peaks are assigned and integrated.

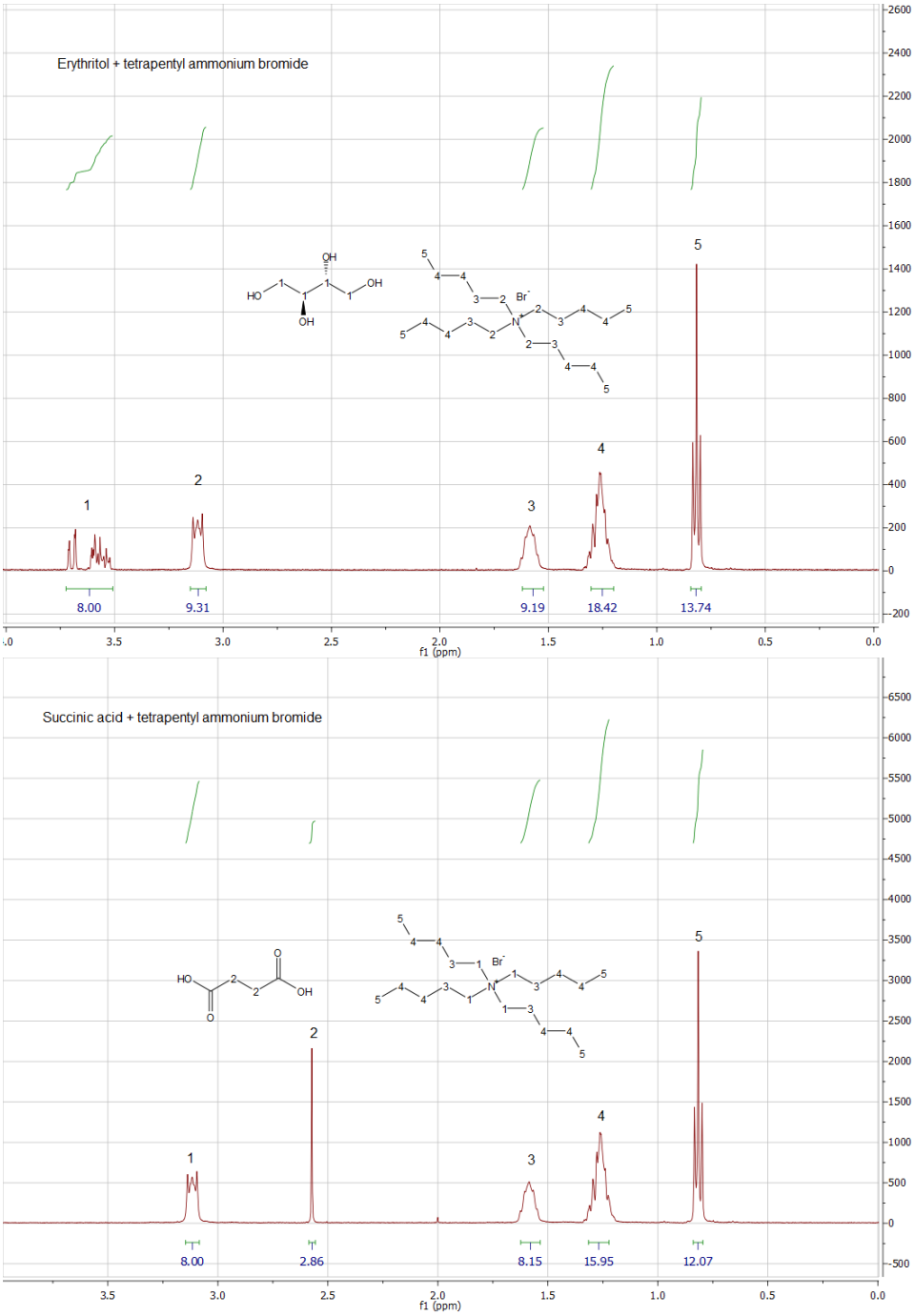

Figure SI 1. Typical NMR spectra of the binary mixtures studied with assigned and integrated peaks indicated. Top: eryhtritol–tetrapentylammonium bromide; x_{TPAB}: 0.575. Bottom: succinic acid–tetrapentylammonium bromide; x_{TPAB}: 0.583.

Table SI 1. Characteristics of the individual components

Name	CAS	Supplier	Product number	Grade	Water content [ppm]
Succinic acid	110-15-6	Sigma-Aldrich	797987-500g	>99%	6.1
Erythritol	149-32-6	Sigma-Aldrich	E7500-100g	>99%	7.7
Tetrapentyl-ammonium bromide	866-97-7	Sigma-Aldrich	241970-25g	>99%	7.3

Table SI 2. Physical and fusion properties of the individual components.

Name	Molar Mass [g/mol]	Density [g/cm^3]	$T_\mathrm{m}^\mathrm{onset}$ [K] (1 K·min^{-1})	$T_\mathrm{m}^\mathrm{endset}$ [K] (1 K·min^{-1})	ΔH_fus [J/mol]
Succinic acid	118.09	1.5595	457.02	460.02	37105.1
Erythritol	122.12	1.4595	391.79	394.66	39300.7
Tetrapentyl-ammonium bromide	378.47	1.0996	373.94	375.91	40140.5

Table SI 3. Literature values for the fusion properties.

Name	T_m, lowest in literature [K]	T_m, highest in literature [K]	T_m, commonly used in literature [K]
Succinic acid	452.15[1]	464.15[2]	460.99[3]
Erythritol	389.35[4]	406.85[5]	392.15[6]
Tetrapentyl-ammonium bromide	369.15[7]	376.15[8]	373.15[9–12]

2. Thermograms of individual components

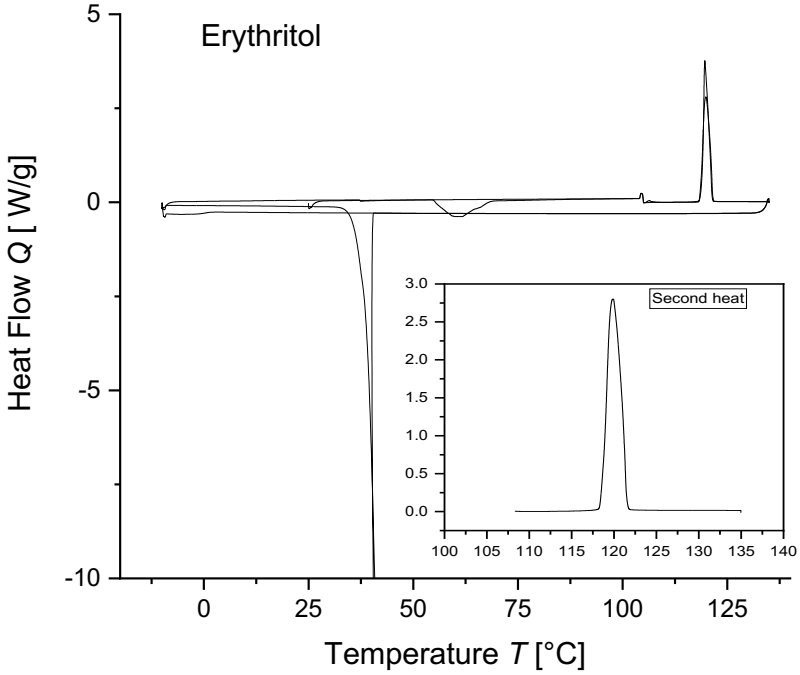

Figure SI 2. Thermogram of erythritol. The graph shows two consecutive runs, the inset shows the fusion peak during the second heating. Cooling and heating until 105 °C performed at a rate of 10 K·min^{-1}. From 105 °C until 135 °C a rate of 1 K·min^{-1} was used, upon heating only.

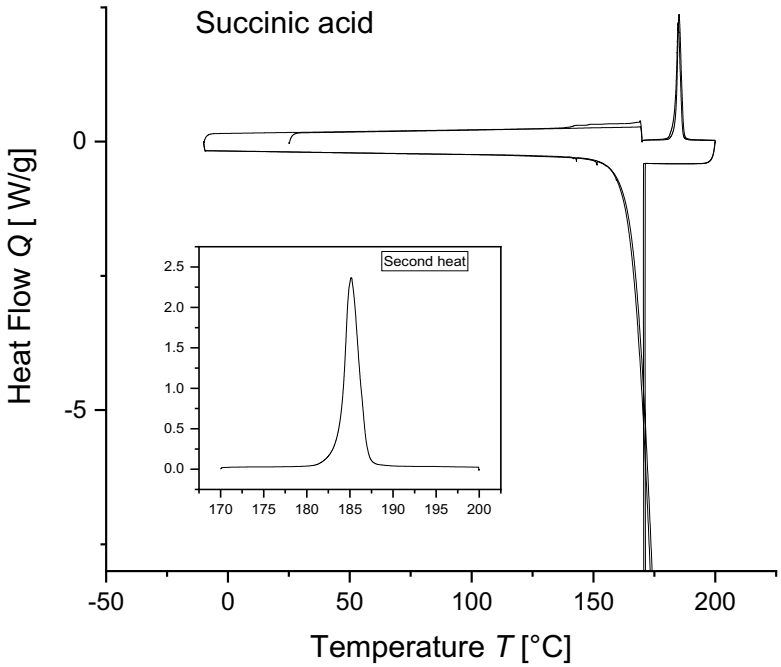

Figure SI 3. Thermogram of succinic acid. The graph shows two consecutive runs, the inset shows the fusion peak during the second heating. Cooling and heating until 170 °C performed at a rate of 10 K·min^{-1}. From 170 °C until 200 °C a rate of 1 K·min^{-1} was used, upon heating only.

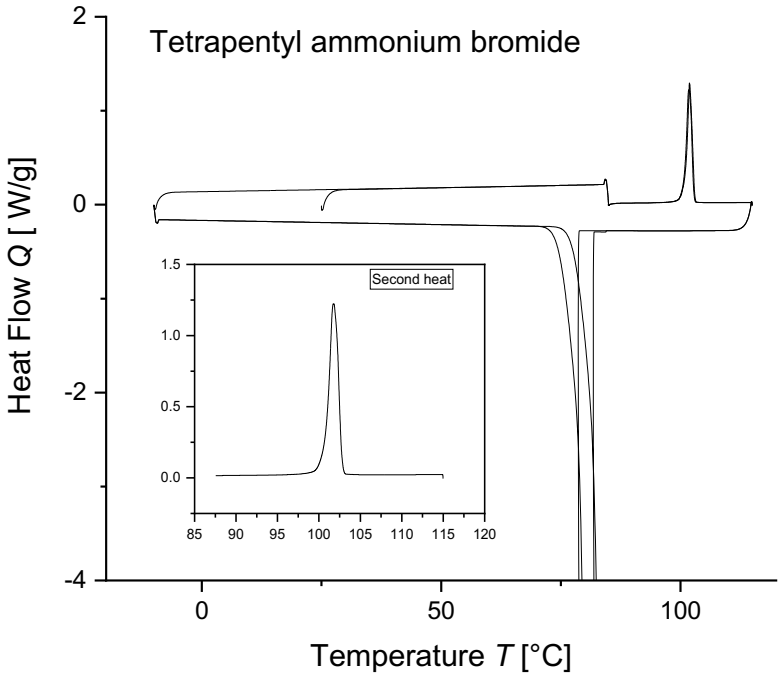

Figure SI 4. Thermogram of tetrapentylammonium bromide. The graph shows two consecutive runs, the inset shows the fusion peak during the second heating. Cooling and heating until 85 °C performed at a rate of 10 K·min^{-1}. From 85 °C until 115 °C a rate of 1 K·min^{-1} was used, upon heating only.

3. Binary phase diagram data

Table SI 4. Liquidus and solidus data for erythritol–tetrapentylammonium bromide. Compositions (x) are given as mole fractions of tetrapentylammonium bromide. T_{data} are measured points. T_{fit} are calculated points with the value of the interaction parameter χ as indicated.

Experimental Data			Fit with: χ: -2.59		Fit with: χ: -2.61	
x	T_{data} [°C]	T_{data} [K]	T_{fit} [K]	$(T_{fit} - T_{data})^2$	T [K]	$(T_{fit} - T_{data})^2$
Liquidus data						
0.000	122.68	395.83	394.66	1.38	394.66	1.38
0.000	120.42	393.57	394.66	1.20	394.66	1.20
0.000	121.02	394.17	394.66	0.24	394.66	0.24
0.000	120.83	393.98	394.66	0.46	394.66	0.46
0.077	120.70	393.85	391.55	5.30	391.54	5.31
0.077	119.75	392.90	391.55	1.83	391.54	1.84
0.092	120.13	393.28	390.81	6.10	390.81	6.13
0.092	120.62	393.77	390.81	8.72	390.81	8.76
0.092	120.62	393.77	390.81	8.72	390.81	8.76
0.110	119.80	392.95	389.83	9.76	389.82	9.81
0.110	119.45	392.60	389.83	7.70	389.82	7.74
0.237	106.90	380.05	381.40	1.82	381.37	1.73
0.237	106.65	379.80	381.40	2.56	381.37	2.45
0.239	107.12	380.27	381.28	1.02	381.24	0.95
0.239	106.72	379.87	381.28	1.99	381.24	1.89
0.283	106.00	379.15	377.66	2.23	377.61	2.37
0.283	106.20	379.35	377.66	2.86	377.61	3.03
0.292	106.00	379.15	376.87	5.18	376.82	5.41
0.292	106.30	379.45	376.87	6.63	376.82	6.90
0.295	105.90	379.05	376.57	6.13	376.52	6.39
0.399	93.77	366.92	366.51	0.16	366.42	0.25
0.399	97.72	370.87	366.51	18.98	366.42	19.77
0.399	94.85	368.00	366.51	2.22	366.42	2.50
0.399	96.67	369.82	366.51	10.93	366.42	11.54
0.498	85.32	358.47	355.16	10.97	355.02	11.86
0.506	81.28	354.43	354.16	0.07	354.02	0.17

0.506	81.90	355.05	354.16	0.79	354.02	1.05
0.581	72.37	345.52	344.52	0.99	344.35	1.35
0.581	72.23	345.38	344.52	0.74	344.35	1.06
0.594	68.85	342.00	342.75	0.56	342.57	0.33
0.594	72.75	345.90	342.75	9.94	342.57	11.07
0.748	84.48	357.63	363.05	29.38	363.02	29.00
0.748	84.72	357.87	363.05	26.90	363.02	26.54
0.752	85.98	359.13	363.33	17.62	363.30	17.34
0.752	85.80	358.95	363.33	19.19	363.30	18.90
0.800	89.23	362.38	366.58	17.65	366.56	17.46
0.800	89.63	362.78	366.58	14.45	366.56	14.28
0.772	89.73	362.88	364.77	3.55	364.74	3.44
0.772	91.13	364.28	364.77	0.23	364.74	0.21
0.896	96.57	369.72	371.91	4.80	371.90	4.77
0.896	96.55	369.70	371.91	4.87	371.90	4.84
0.907	97.82	370.97	372.43	2.15	372.43	2.13
0.907	97.97	371.12	372.43	1.73	372.43	1.72
1.000	101.87	375.02	375.91	0.80	375.91	0.80
1.000	101.60	374.75	375.91	1.35	375.91	1.35
1.000	101.60	374.75	375.91	1.35	375.91	1.35
Solidus data						
0.077	72.50	345.65	347.00	1.82	346.86	1.46
0.100	72.07	345.22	347.00	3.18	346.86	2.70
0.100	73.12	346.27	347.00	0.54	346.86	0.35
0.100	71.65	344.80	347.00	4.84	346.86	4.24
0.100	72.70	345.85	347.00	1.32	346.86	1.02
0.200	72.07	345.22	347.00	3.18	346.86	2.70
0.200	71.03	344.18	347.00	7.93	346.86	7.16
0.200	71.65	344.80	347.00	4.84	346.86	4.24
0.200	72.70	345.85	347.00	1.32	346.86	1.02
0.237	72.92	346.07	347.00	0.87	346.86	0.63
0.283	72.92	346.07	347.00	0.87	346.86	0.63
0.290	72.07	345.22	347.00	3.18	346.86	2.70
0.290	72.28	345.43	347.00	2.45	346.86	2.04
0.290	72.07	345.22	347.00	3.18	346.86	2.70

0.290	72.70	345.85	347.00	1.32	346.86	1.02
0.399	72.92	346.07	347.00	0.87	346.86	0.63
0.498	72.92	346.07	347.00	0.87	346.86	0.63
0.594	72.92	346.07	347.00	0.87	346.86	0.63
0.700	73.75	346.90	347.00	0.01	346.86	0.00
0.748	77.90	351.05	347.00	16.40	346.86	17.56
0.748	76.32	349.47	347.00	6.08	346.86	6.79
0.748	76.23	349.38	347.00	5.68	346.86	6.37
0.748	73.98	347.13	347.00	0.02	346.86	0.07
0.775	73.75	346.90	347.00	0.01	346.86	0.00
0.800	76.23	349.38	347.00	5.68	346.86	6.37
0.800	76.65	349.80	347.00	7.84	346.86	8.64
0.800	75.82	348.97	347.00	3.87	346.86	4.44
0.800	76.82	349.97	347.00	8.80	346.86	9.65
0.900	74.57	347.72	347.00	0.51	346.86	0.73
0.900	76.57	349.72	347.00	7.38	346.86	8.16
0.900	75.82	348.97	347.00	3.87	346.86	4.44
0.900	75.65	348.80	347.00	3.24	346.86	3.76

Table SI 5. Liquidus and solidus data for succinic acid–tetrapentylammonium bromide. Compositions (x) are given as mole fractions of tetrapentylammonium bromide. T_{data} are measured points. T_{fit} are calculated points with the value of the interaction parameter χ as indicated.

Experimental Data			Fit with: χ: -4.68		Fit with: χ: -5.15	
x	T_{fit} [°C]	T_{data} [K]	T_{fit} [K]	$(T_{fit} - T_{data})^2$	T [K]	$(T_{fit} - T_{data})^2$
Liquidus data						
0.000	184.8	457.92	460.02	4.42	460.02	4.42
0.000	183.7	456.83	460.02	10.15	460.02	10.15
0.155	173.9	447.02	447.07	0.00	446.57	0.20
0.155	168.0	441.10	447.07	35.69	446.57	29.91
0.187	173.5	446.68	443.10	12.81	442.38	18.49
0.187	168.8	441.93	443.10	1.37	442.38	0.20
0.306	148.5	421.67	424.80	9.82	423.03	1.85
0.311	148.9	422.08	424.03	3.78	422.21	0.02
0.311	144.6	417.73	424.03	39.63	422.21	20.04
0.394	119.0	392.13	408.36	263.21	405.65	182.68
0.394	120.2	393.37	408.36	224.72	405.65	150.86
0.396	117.3	390.47	408.02	308.14	405.29	219.85
0.396	122.6	395.78	408.02	149.75	405.29	90.45
0.591	85.3	358.42	365.00	43.40	360.18	3.09
0.591	85.1	358.27	365.00	45.40	360.18	3.64
0.606	84.8	357.92	361.43	12.38	356.46	2.12
0.606	85.3	358.43	361.43	9.01	356.46	3.89
0.706	87.8	360.97	355.07	34.75	354.01	48.37
0.706	87.6	360.77	355.07	32.44	354.01	45.63
0.700	87.9	361.03	354.44	43.43	353.35	59.10
0.700	87.4	360.53	354.44	37.09	353.35	51.66
0.850	92.5	365.63	368.25	6.84	367.95	5.38
0.850	90.5	363.68	368.25	20.84	367.95	18.22
0.800	90.9	364.03	364.27	0.06	363.76	0.08
0.800	90.6	363.78	364.27	0.24	363.76	0.00
0.962	98.2	371.38	374.60	10.34	374.58	10.22
0.962	98.5	371.60	374.60	8.99	374.58	8.88
0.927	97.4	370.53	372.97	5.93	372.89	5.58

0.927	98.1	371.20	372.98	3.17	372.91	2.92
1.000	101.9	375.05	375.91	0.74	375.91	0.74
1.000	101.6	374.75	375.91	1.35	375.91	1.35
Solidus data						
0.155	73.3	346.48	349.27	7.77	346.62	0.02
0.306	74.2	347.32	349.27	3.82	346.62	0.49
0.396	75.4	348.57	349.27	0.49	346.62	3.79
0.514	75.4	348.57	349.27	0.49	346.62	3.79
0.606	75.4	348.57	349.27	0.49	346.62	3.79
0.700	79.2	352.32	349.27	9.28	346.62	32.45
0.927	77.9	351.07	349.27	3.23	346.62	19.77
0.964	78.8	351.90	349.27	6.92	346.62	27.88
0.187	73.8	346.90	349.27	5.62	346.62	0.08
0.311	73.8	346.90	349.27	5.62	346.62	0.08
0.394	75.0	348.15	349.27	1.25	346.62	2.34
0.525	75.4	348.57	349.27	0.49	346.62	3.79
0.591	75.8	348.98	349.27	0.08	346.62	5.59
0.700	78.8	351.90	349.27	6.92	346.62	27.88
0.927	78.3	351.48	349.27	4.90	346.62	23.65
0.981	77.5	350.65	349.27	1.90	346.62	16.24

4. References

1. Dallacker, F. & Schmets, G. Über die Darstellung von Dimethoxy-methylendioxy-benzol-dicarbonsäuren. *Chem. Ber.* **104,** 2534–2544 (1971).

2. Dean, F. M., Roberts, J. C. & Robertson, A. The Chemistry of Pungi. Part X X I P Nidulin and Nornidulin (" Ustin ") : Chlorine-containing Metabolic Products of. *J. Chem. Soc.* 1432–1439 (1954). doi:10.1039/JR9540001432

3. Thalladi, V. R., Nüsse, M. & Boese, R. The melting point alternation in α,ω-alkanedicarboxylic acids. *J. Am. Chem. Soc.* **122,** 9227–9236 (2000).

4. Mueller, A. H. R. Über total instabile Formen. *Zeitschrift für Phys. Chemie* **86,** 215 (1914).

5. Fujii, K. *et al.* Physical Characterization of meso-Erythritol as a Crystalline Bulking Agent for Freeze-Dried Formulations. *Chem. Pharm. Bull* **63,** 311–317 (2015).

6. Suzuki, H. & Sunada, H. Comparision of Nicotinamide, Ethylurea, and Polyethylene Glycole as Carriers for Nifedipine Solid Dispersion Systems. *Chem. Pharm. Bull.* **45,** 1688–1693 (1997).

7. Kellet, Jr., J. C. & Doggett, W. C. Cholinergic Anionic Receptors. *J. Pharm. Sci.* **55,** 414–417 (1966).

8. Coker, T. G., Ambrose, J. & Janz, G. J. Fusion Properties of Some Ionic Quaternary Ammonium Compounds. *J. Am. Chem. Soc.* **92,** 5293–5297 (1970).

9. Nakayama, H. Solid-Liquid and Liquid-Liquid Phase Equilibria in the Symmetrical Tetraalkylammonium Halide–Water Systems. *Bulletin of the Chemical Society of Japan* **54,** 3717–3722 (1981).

10. McDowell, M. J. & Kraus, C. A. Properties of Electrolytic Solutions. XXVIII. Conductance of Some Salts in Nitrobenzene at 25°. *J. Am. Chem. Soc.* **73,** 3293–3294 (1951).

11. Daggett, H. M., Bair, E. J. & Kraus, C. A. Properties of Electrolytic Solutions. XLVII. Conductance of Some Quaternary Ammonium and Other Salts in Water at Low Concentration. *J. Am. Chem. Soc.* **73,** 799–803 (1951).

12. Goodrich, J. C., Goyan, F. M., Morse, E. E., Preston, R. G. & Young, M. B. Applications of the Eastman Thermocell Equation. I. Certain Absolute Ionic Entropies and Entropies of Transfer of Alkali Metal and Tetraalkylammomum Bromides and Hydroxides. *J. Am. Chem. Soc.* **72,** 4411–4418 (1950).