Thermodynamic model for methanesulfonic acid recovery by tri-n-butyl phosphate

Rayco Lommelen,[a*] Charlotte Lempereur,[a†] and Koen Binnemans[a]

[a]KU Leuven, Department of Chemistry, Celestijnenlaan 200F, P.O. box 2404, B–3001 Leuven, Belgium

* Corresponding author: Email: rayco.lommelen@kuleuven.be

Supplementary Information (SI)

† New address: Université Grenoble Alpes, Université Savoie Mont-Blanc, CNRS, Grenoble INP, LEPMI, 38000 Grenoble, France

1. Experimental details and results

Explanation for abbreviations in tables:

- a = aqueous phase
- o = organic phase
- in = initial
- e = equilibrium
- ρ = density
- *O/A* = organic to equation volumetric ratio
- D_{MSA} = distribution ratio = $\frac{[\mathrm{MSA}]_{\mathrm{o,e}}}{[\mathrm{MSA}]_{\mathrm{a,e}}}$
- E_{MSA} = extraction efficiency = $\frac{[\mathrm{MSA}]_{\mathrm{o,e}} \cdot (O/A)_e}{[\mathrm{MSA}]_{\mathrm{aq,in}}} \cdot 100$
- L_{MSA} = extractant loading = $\frac{[\mathrm{MSA}]_{\mathrm{o,e}} \cdot (O/A)_e}{[\mathrm{TBP}]_{\mathrm{o,in}}} \cdot 100$

The following equation can be used to convert the TBP concentration in *n*-dodecane from wt% to vol%:

$$[\mathrm{TBP}]\ (vol\%) = \frac{[\mathrm{TBP}]\ (wt\%) \ / \ \rho_{TBP}}{[\mathrm{TBP}]\ (wt\%) \ / \ \rho_{TBP} + [\mathrm{dodecane}\ ]\ (wt\%) \ / \ \rho_{dodecane}}$$

with ρ_{TBP} = 973 g L^{-1} and $\rho_{dodecane}$ = 750 g L^{-1}.

Table S1. Experimental details for MSA–100 vol% TBP system collected at 25 °C with O/A_{in} = 1.

$[MSA]_{a,in}$ mol L^{-1}	$[MSA]_{a,e}$ mol L^{-1}	$[MSA]_{o,e}$ mol L^{-1}	ρ_o g mL^{-1}	$[H_2O]_o$ mol L^{-1}	$(O/A)_e$	D_{MSA}	E_{MSA} %	L_{MSA} %
0.00	0.00	0.00	0.976	3.70	1.13			
0.10	0.10		0.976	3.60				
0.25	0.25	0.00	0.976	3.48	1.18	0.008	0.93	0.1
0.49	0.51	0.01	0.976	3.55	1.12	0.013	1.39	0.2
0.74	0.76	0.01	0.976	3.69	1.13	0.018	1.97	0.4
0.98	1.01	0.02	0.977	3.63	1.13	0.024	2.57	0.7
1.96	1.96	0.11	0.981	3.89	1.15	0.056	5.95	3.2
2.96	2.79	0.29	0.989	4.44	1.20	0.104	10.69	8.7
3.94	3.60	0.66	1.006	5.40	1.33	0.184	19.14	20.9
4.93	4.35	1.09	1.024	6.42	1.49	0.249	26.37	35.9
5.92	5.34	1.67	1.046	7.57	1.80	0.313	36.39	59.5
7.89	6.82	2.83	1.093	8.76	2.65	0.415	52.12	117
9.86	7.20	4.62	1.160	9.32	7.35	0.642	82.53	225.

Table S2. Experimental details for MSA–TBP–dodecane system collected at 25 °C with O/A_{in} = 1. $[n\text{-dodecane}]_{o,in}$ (wt%) = 100% - $[TBP]_{o,in}$

$[MSA]_{a,in}$ mol L^{-1}	$[TBP]_{o,in}$ wt%	$[MSA]_{a,e}$ mol L^{-1}	$[MSA]_{o,e}$ mol L^{-1}	ρ_o g mL^{-1}	$[H_2O]_o$ mol L^{-1}	$(O/A)_e$	D_{MSA}	E_{MSA} %	L_{MSA} %
0.25	50.2			0.844	0.87				
0.25	60.2	0.25	0.00	0.865	1.21	1.04	0.001	0.1	0.0
0.25	69.6	0.25	0.00	0.891	1.51	1.05	0.002	0.2	0.0
0.25	79.5	0.25	0.00	0.917	1.99	1.06	0.003	0.3	0.0
0.25	89.8	0.25	0.00	0.945	2.62	1.09	0.006	0.6	0.0
0.25	95.0	0.25	0.00	0.961	3.05	1.10	0.007	0.7	0.1
1.97	50.2	1.98	0.01	0.844	0.73	1.02	0.004	0.4	0.6
1.97	60.2	2.06	0.01	0.865	1.02	1.04	0.007	0.7	0.7
1.97	69.6	2.07	0.02	0.892	1.38	1.04	0.012	1.2	1.1
1.97	79.5	1.97	0.04	0.919	1.94	1.07	0.020	2.0	1.5
1.97	89.8	2.05	0.07	0.948	2.58	1.09	0.032	3.5	2.2
1.97	95.0	2.02	0.09	0.964	3.00	1.11	0.042	4.5	2.7
3.91	50.2	3.93	0.06	0.848	0.78	1.03	0.016	1.6	4.0
3.91	60.2	3.94	0.10	0.870	1.19	1.06	0.026	2.7	5.5
3.91	69.6	3.67	0.16	0.899	1.67	1.07	0.042	4.1	7.0
3.91	79.5	3.90	0.28	0.930	2.68	1.13	0.073	7.7	11.1
3.91	89.8	3.76	0.41	0.964	3.71	1.12	0.110	11.5	14.3
3.91	95.0	3.70	0.50	0.983	4.45	1.25	0.135	14.2	16.4
5.87	89.8	5.94	1.33	1.004	5.78	1.53	0.223	27.4	50.9
5.87	95.0	5.82	1.51	1.022	6.89	1.70	0.259	32.4	56.1
7.82	89.8	7.64	2.58	1.070	7.93	2.20	0.337	45.3	112
7.82	95.0	7.61	2.61	1.070	7.99	2.36	0.342	46.8	108
9.78	95.0	8.84	4.38	1.143	8.86	5.42	0.496	75.7	219

Table S3. Experimental details for MSA–100 vol% TBP system with O/A_{in} = 1.

$[MSA]_{a,in}$ mol L^{-1}	T °C	$[MSA]_{aq,e}$ mol L^{-1}	$[MSA]_{org,e}$ mol L^{-1}	$[H_2O]_{org}$ mol L^{-1}	$(O/A)_e$	D_{MSA}	E_{MSA} %	L_{MSA} %
2.02	24	2.04	0.11		*1.13* [a]	0.052	*5.5* [a]	*3.1* [a]
2.02	40	2.13	0.06		*1.11* [a]	0.030	*3.4* [a]	*1.9* [a]
2.02	59	2.13	0.05		*1.11* [a]	0.024	*2.7* [a]	*1.5* [a]
2.02	77	2.14	0.04		*1.11* [a]	0.019	*2.1* [a]	*1.2* [a]
4.01	24	4.04	0.66		*1.38* [a]	0.163	*19* [a]	*21* [a]
4.01	40	4.12	0.52		*1.27* [a]	0.125	*14* [a]	*16* [a]
4.01	59	4.25	0.35		*1.21* [a]	0.081	*10* [a]	*10* [a]
4.01	77	4.27	0.35		*1.20* [a]	0.081	*10* [a]	*11* [a]
6.01	24	5.74	1.67	7.78	1.843	0.290	35.9	32.4
6.01	40	5.79	1.51	6.59	1.645	0.260	31.1	31.5
6.01	59	5.66	1.17	3.22	1.305	0.207	22.0	28.1
6.01	77	5.92	1.16	2.05	1.250	0.196	21.4	28.4
8.01	24	7.42	2.97		*2.56* [a]	0.400	*52* [a]	*114* [a]
8.01	40	7.49	2.83		*2.05* [a]	0.378	*45* [a]	*101* [a]
8.01	59	7.33	2.38		*1.71* [a]	0.324	*35* [a]	*78* [a]
8.01	77	7.15	2.32		*1.59* [a]	0.324	*33* [a]	*73* [a]

[a] Determined based on equilibrium volumes calculated by the thermodynamic model

Table S4. Experimental details for MSA–$Ni(CH_3SO_3)_2$–100 vol% TBP at 25 °C with O/A_{in} = 1.

$[MSA]_{a,in}$ mol L^{-1}	$[Ni(MSA)_2]_{a,in}$ mol L^{-1}	$[MSA]_{aq,e}$ mol L^{-1}	$[MSA]_{org,e}$ mol L^{-1}	ρ_o g mL^{-1}	$[H_2O]_{org}$ mol L^{-1}	$(O/A)_e$	D_{MSA}	E_{MSA} %	L_{MSA} %
4.60	0.00	4.48	0.92	1.015	6.46	1.56	0.205	24.4	30.9
4.60	0.26	4.33	1.10	1.022	6.69	1.63	0.253	29.6	37.5
4.60	0.53	4.04	1.19	1.026	6.55	1.63	0.295	32.1	40.7
4.60	0.79	3.82	1.34	1.032	6.62	1.67	0.350	36.4	46.0
4.60	1.05	3.59	1.48	1.041	6.49	1.78	0.412	41.1	52.1
4.60	1.31	3.36	1.60	1.042	6.22	1.78	0.475	44.5	56.4
4.60	1.47	3.17	1.65	1.048	6.06	1.78	0.522	46.0	58.3
7.66	0.00	7.06	2.87	1.085	9.21	2.61	0.407	52.8	112
7.66	0.26	6.40	2.94	1.089	8.51	2.75	0.460	54.9	116
7.66	0.53	6.36	3.04	1.094	7.75	2.92	0.479	58.0	123

2. Thermodynamic model fits to experimental data

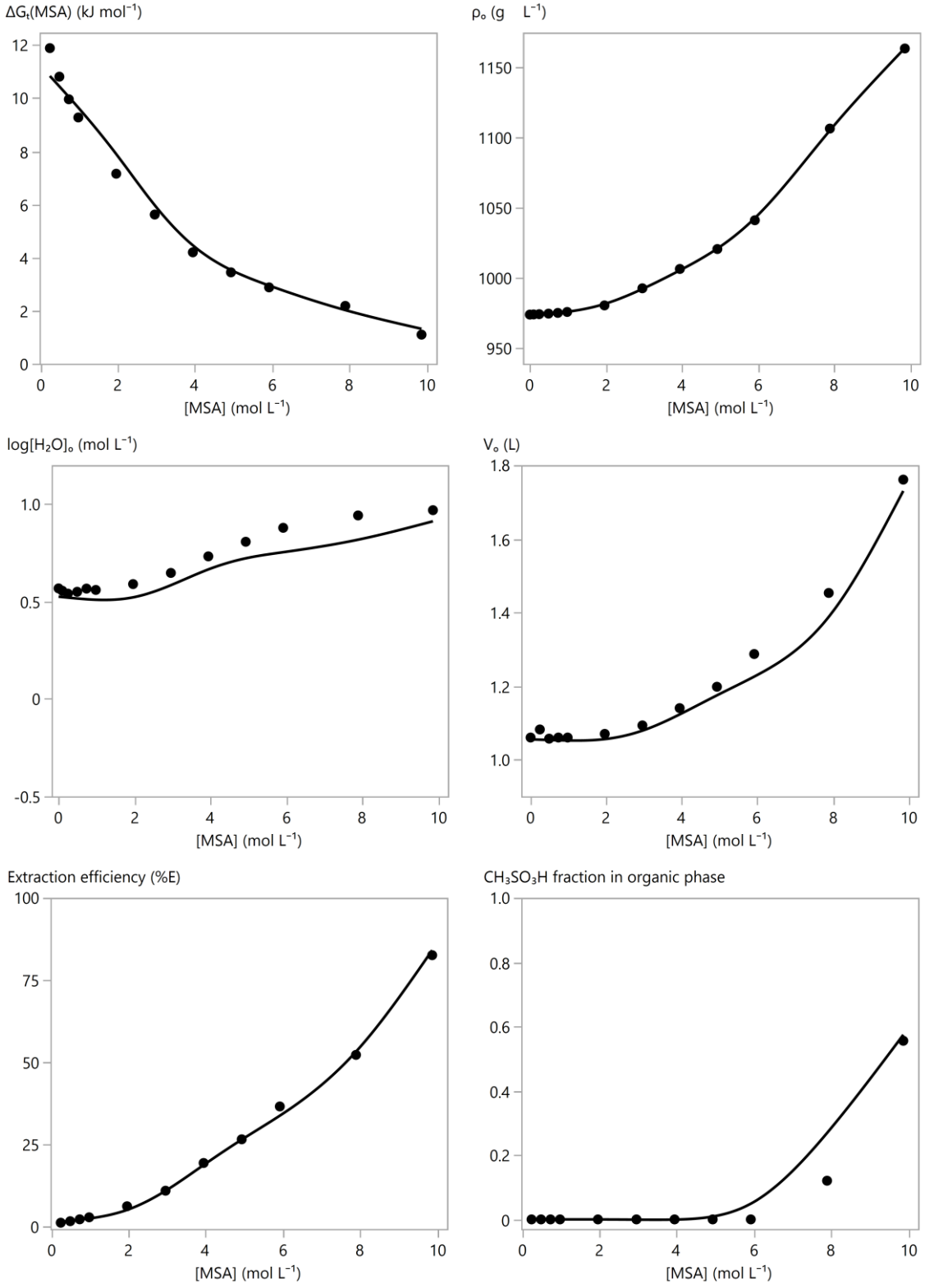


Figure S1. Model fit (lines) to experimental data (markers) with undiluted TBP at 25 °C from Table S1. Experimental CH_3SO_3H values are based on %L.

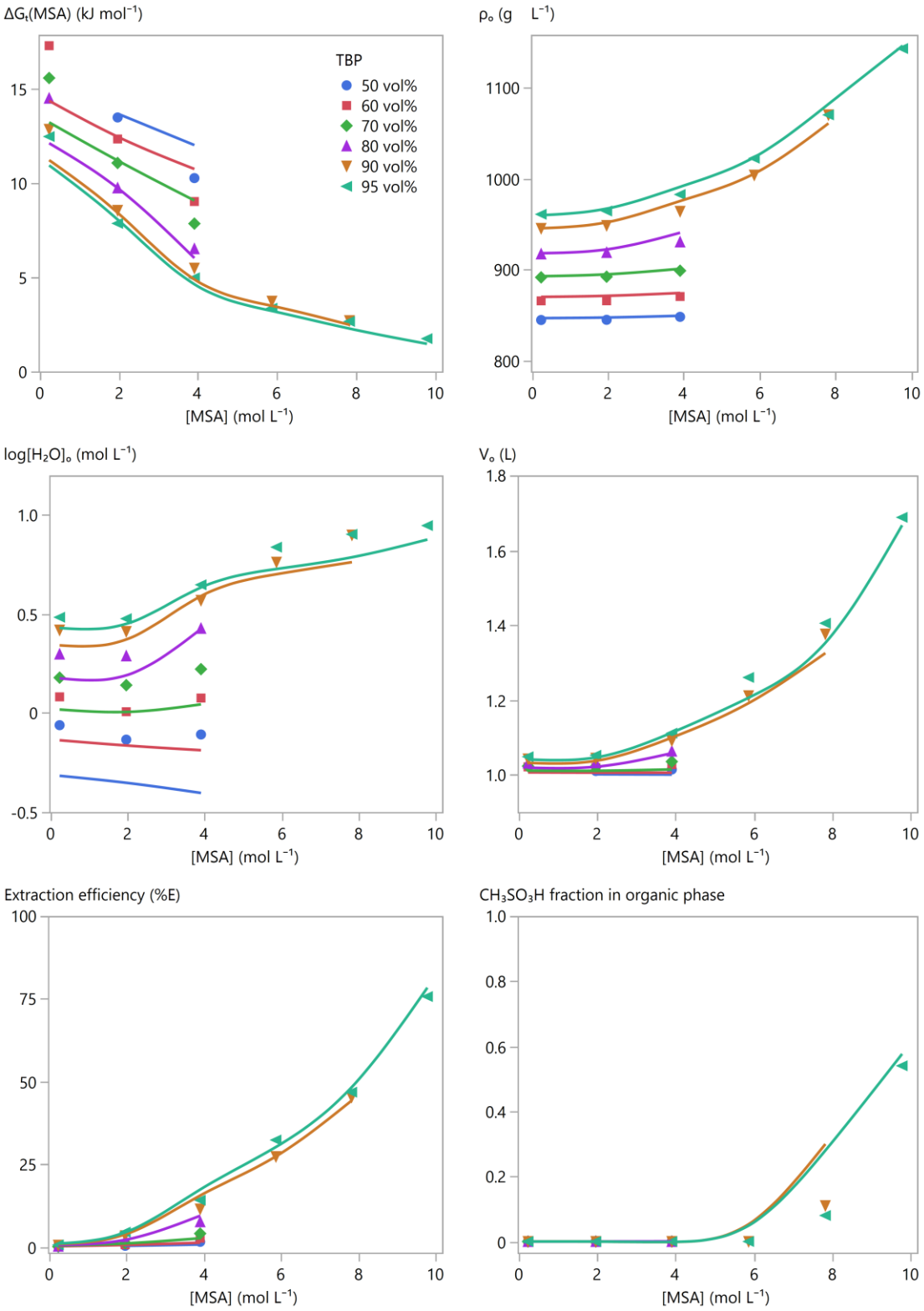


Figure S2. Model fit (lines) to experimental data (markers) with diluted TBP at 25 °C from Table S2. Experimental CH_3SO_3H values are based on %L.

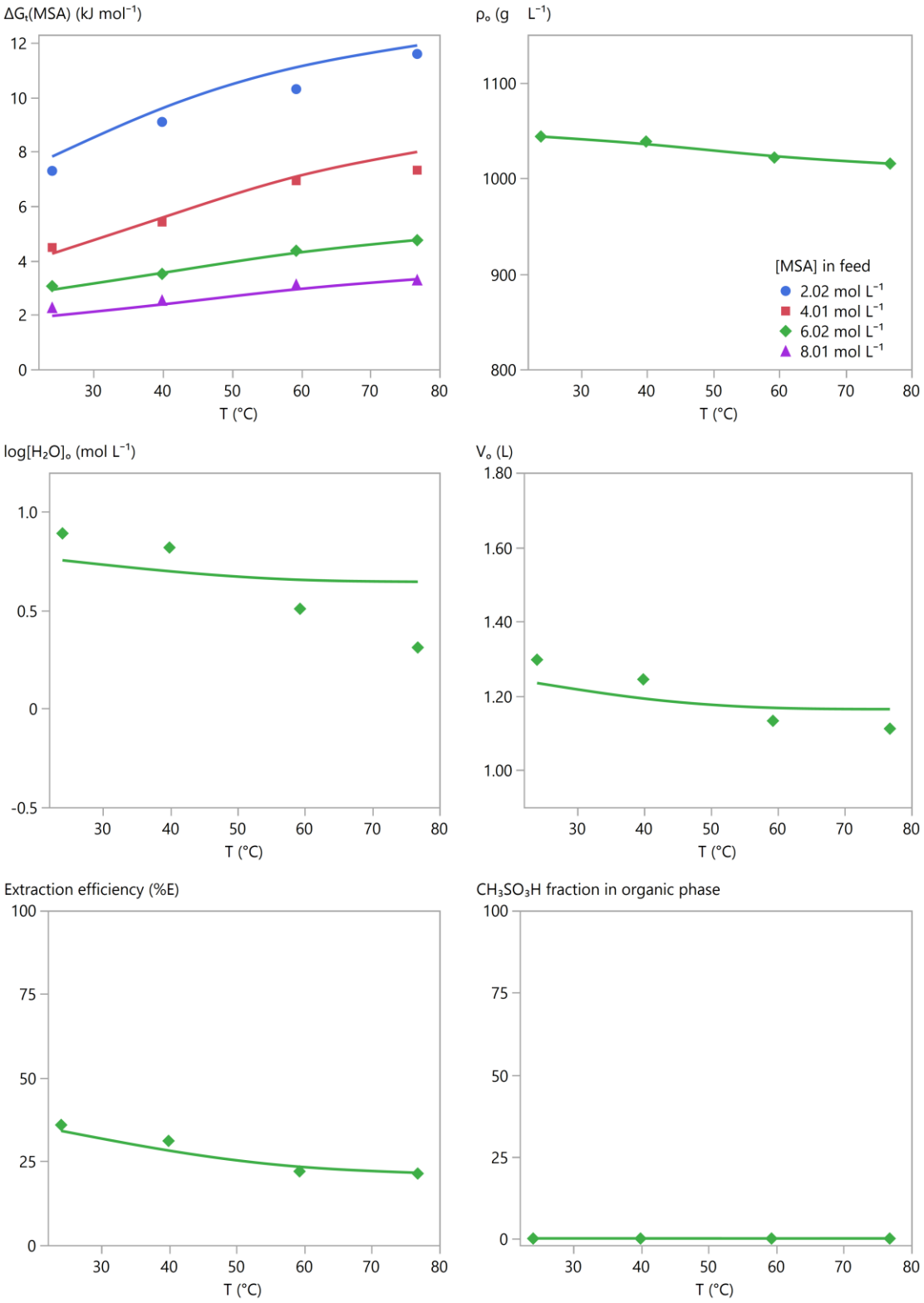


Figure S3. Model fit (lines) to experimental data (markers) with undiluted TBP at different temperatures from Table S1. Experimental CH_3SO_3H values are based on %L.

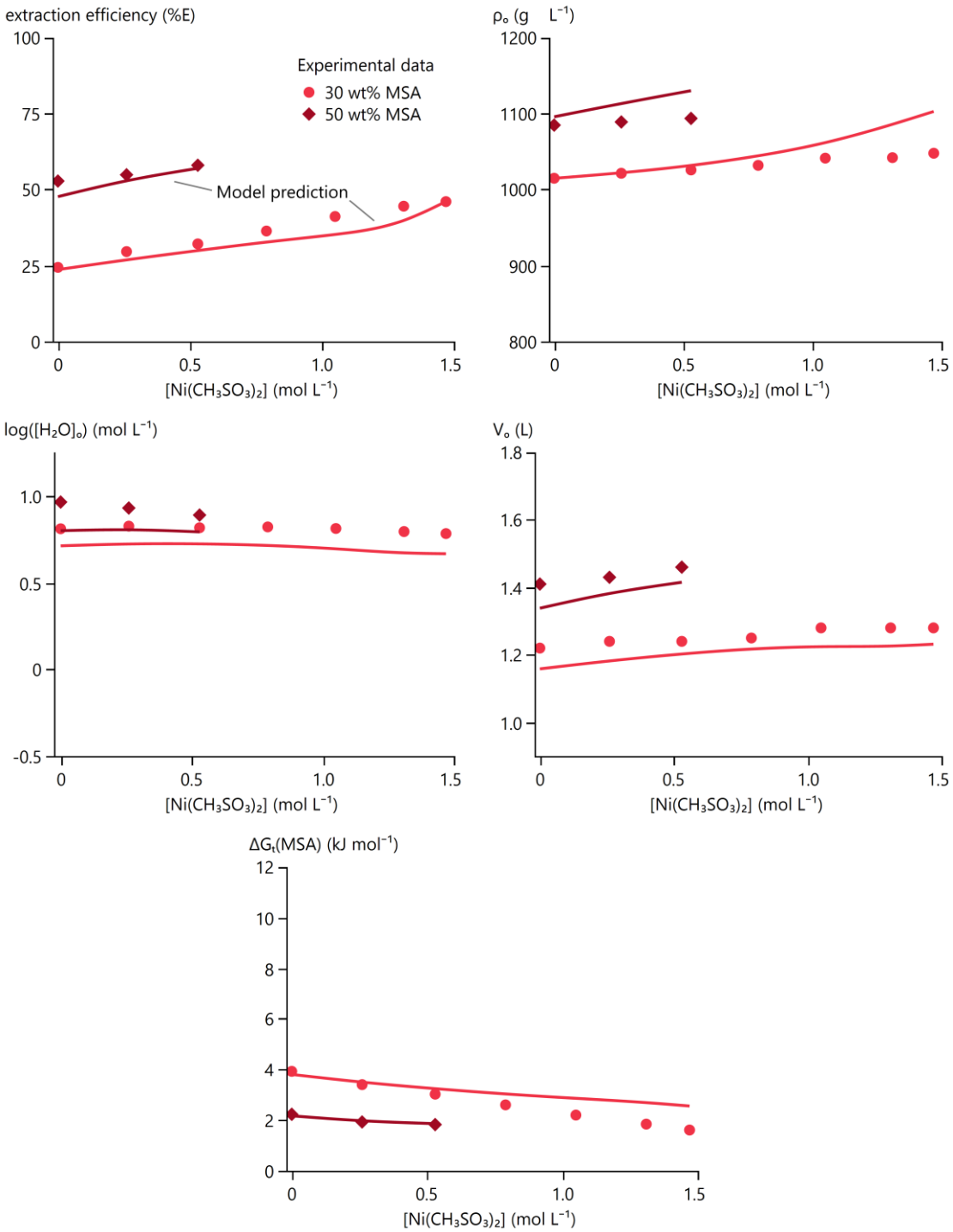
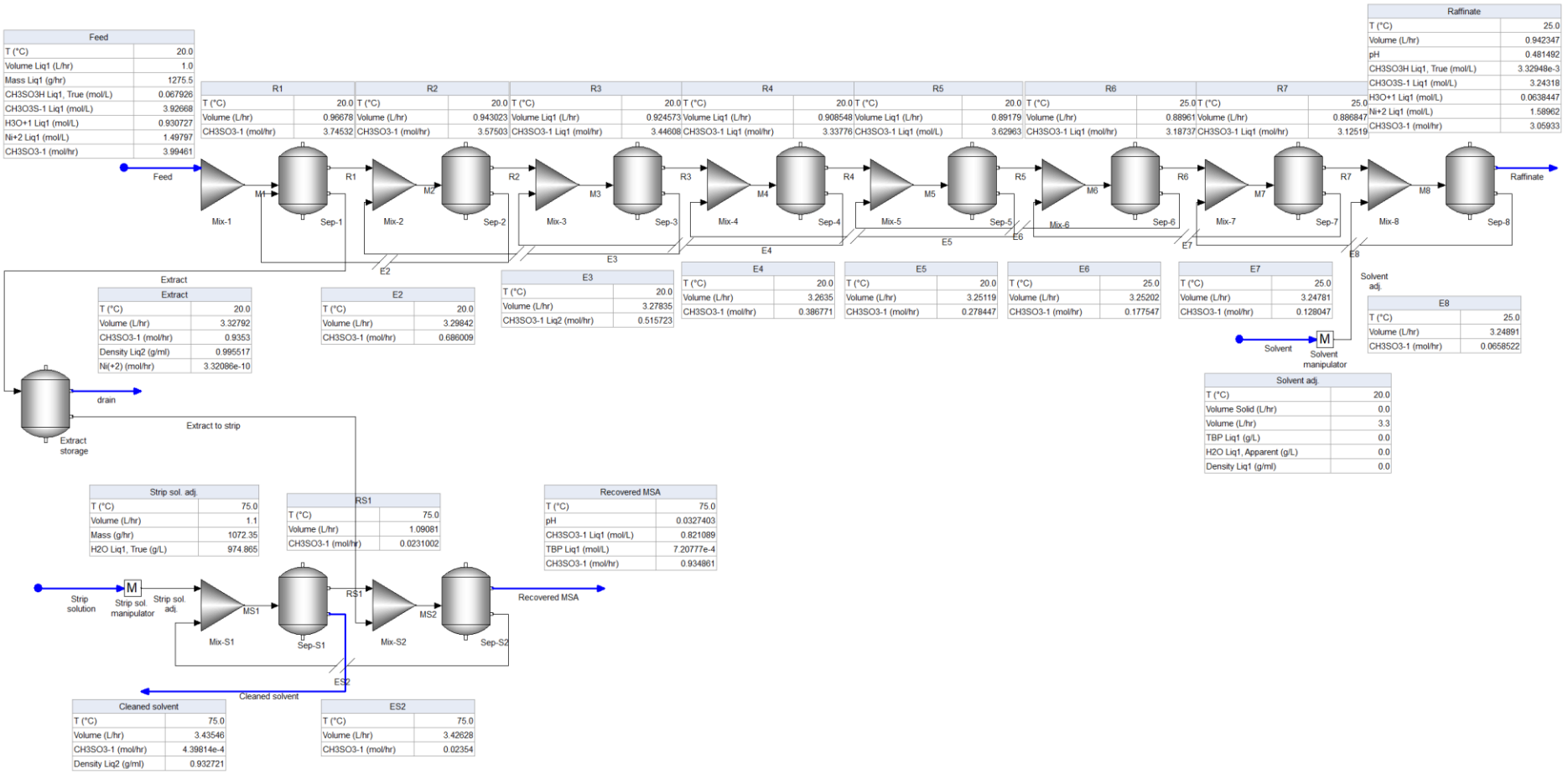


Figure S4. Model fit (lines) to experimental data (markers) on the MSA–$Ni(CH_3SO_3)_2$–H_2O–TBP system at 25 °C from Table S4.

3. Simulation of a solvent extraction process for MSA recovery



Feed	
T (°C)	20.0
Volume Liq1 (L/hr)	1.0
Mass Liq1 (g/hr)	1275.5
CH3SO3H Liq1, True (mol/L)	0.067926
CH3SO3S-1 Liq1 (mol/L)	3.92668
H3O+1 Liq1 (mol/L)	0.930727
Ni+2 Liq1 (mol/L)	1.49797
CH3SO3-1 (mol/hr)	3.99461

R1		R2		R3		R4		R5		R6		R7	
T (°C)	20.0	T (°C)	20.0	T (°C)	20.0	T (°C)	20.0	T (°C)	20.0	T (°C)	25.0	T (°C)	25.0
Volume (L/hr)	0.96678	Volume (L/hr)	0.943023	Volume Liq1 (L/hr)	0.924573	Volume Liq1 (L/hr)	0.908548	Volume Liq1 (L/hr)	0.89179	Volume (L/hr)	0.88961	Volume (L/hr)	0.886847
CH3SO3-1 (mol/hr)	3.74532	CH3SO3-1 (mol/hr)	3.57503	CH3SO3-1 Liq1 (mol/hr)	3.44608	CH3SO3-1 Liq1 (mol/hr)	3.33776	CH3SO3-1 Liq1 (mol/L)	3.62963	CH3SO3-1 Liq1 (mol/hr)	3.18737	CH3SO3-1 Liq1 (mol/hr)	3.12519

Raffinate	
T (°C)	25.0
Volume (L/hr)	0.942347
pH	0.481492
CH3SO3H Liq1, True (mol/L)	3.32948e-3
CH3SO3S-1 Liq1 (mol/L)	3.24318
H3O+1 Liq1 (mol/L)	0.0638447
Ni+2 Liq1 (mol/L)	1.58962
CH3SO3-1 (mol/hr)	3.05933

Extract	
T (°C)	20.0
Volume (L/hr)	3.32792
CH3SO3-1 (mol/hr)	0.9353
Density Liq2 (g/ml)	0.995517
Ni(+2) (mol/hr)	3.32086e-10

E2	
T (°C)	20.0
Volume (L/hr)	3.29842
CH3SO3-1 (mol/hr)	0.686009

E3	
T (°C)	20.0
Volume (L/hr)	3.27835
CH3SO3-1 Liq2 (mol/hr)	0.515723

E4	
T (°C)	20.0
Volume (L/hr)	3.2635
CH3SO3-1 (mol/hr)	0.386771

E5	
T (°C)	20.0
Volume (L/hr)	3.25119
CH3SO3-1 (mol/hr)	0.278447

E6	
T (°C)	25.0
Volume (L/hr)	3.25202
CH3SO3-1 (mol/hr)	0.177547

E7	
T (°C)	25.0
Volume (L/hr)	3.24781
CH3SO3-1 (mol/hr)	0.128047

E8	
T (°C)	25.0
Volume (L/hr)	3.24891
CH3SO3-1 (mol/hr)	0.0658522

Solvent adj.	
T (°C)	20.0
Volume Solid (L/hr)	0.0
Volume (L/hr)	3.3
TBP Liq1 (g/L)	0.0
H2O Liq1, Apparent (g/L)	0.0
Density Liq1 (g/ml)	0.0

Strip sol. adj.	
T (°C)	75.0
Volume (L/hr)	1.1
Mass (g/hr)	1072.35
H2O Liq1, True (g/L)	974.865

RS1	
T (°C)	75.0
Volume (L/hr)	1.09081
CH3SO3-1 (mol/hr)	0.0231002

Recovered MSA	
T (°C)	75.0
pH	0.0327403
CH3SO3-1 Liq1 (mol/L)	0.821089
TBP Liq1 (mol/L)	7.20777e-4
CH3SO3-1 (mol/hr)	0.934861

Cleaned solvent	
T (°C)	75.0
Volume (L/hr)	3.43546
CH3SO3-1 (mol/hr)	4.39814e-4
Density Liq2 (g/ml)	0.932721

ES2	
T (°C)	75.0
Volume (L/hr)	3.42628
CH3SO3-1 (mol/hr)	0.02354

Figure S5. Flowsheet for MSA recovery with 8 extraction and 3 stripping stages developed in OLI Flowsheet version 12.0 from OLI Systems.

4. TBP and *n*-dodecane concentration conversion table

Table S5. Molar amounts and masses of tri-n-butyl phosphate (TBP), and n-dodecane (dod.) that must be mixed to obtain a certain concentration of TBP (in vol.%) in 1 litre of solvent.

TBP (vol%)	n_{TBP} in $n_{dod.}$ (mole)		m_{TBP} in $m_{dod.}$ (g)	
0	0	4.40	0	750
5	0.18	4.18	49	713
10	0.36	3.96	97	675
15	0.55	3.74	146	638
20	0.73	3.52	194	600
25	0.91	3.30	243	563
30	1.09	3.08	292	525
35	1.28	2.86	340	488
40	1.46	2.64	389	450
45	1.64	2.42	437	413
50	1.82	2.20	486	375
60	2.19	1.76	583	300
70	2.55	1.32	680	225
80	2.92	0.88	778	150
90	3.28	0.44	875	75
100	3.65	0.00	972	0