## SUPPLEMENTARY MATERIAL

## **PDMS-Based Membranes**



**Figure A1:** Permeate fluxes of water through different  $Pervap^{TM}$  4060 membranes ( $T = 37 \ ^{\circ}C$ ,  $p_{Perm} = 10 \ mbar$ ). Pervaporation was carried out using binary mixtures of water with butanol (black), acetone (grey) and ethanol (light grey).



**Figure A2:** Permeate fluxes through Pervap<sup>TM</sup> 4060 membranes, determined for varying A:B:E ratios in the feed (T = 37 °C,  $p_{Perm} = 10 \text{ mbar}$ ). (**A**) permeate fluxes of butanol (black) and water (grey); (**B**) permeate fluxes of acetone (grey) and ethanol (light grey).



**Figure A3:** Butanol permeate concentrations determined with  $Pervap^{TM}$  4060 membranes for varying temperatures (black = 37 °C; grey = 50 °C; bright grey = 60 °C) and permeate pressures (10 mbar to 80 mbar). Feed mixtures contained acetone, butanol and ethanol in a 3:6:1 ratio.



**Figure A4:** Comparison of permeate concentrations of butanol (black), acetone (grey) and ethanol (bright grey) obtained with the commercially available Pervap<sup>TM</sup> 4060 membranes and the silicone membrane produced by our group (Silicone-FVT).

## **PEBA Membranes**

b<sub>21</sub>[K]

C<sub>12</sub>[-]

228.279

0.3



**Figure A5:** Butanol permeate concentrations determined with PEBA membranes for varying temperatures (dark grey =  $37 \degree$ C; grey =  $50 \degree$ C; bright grey =  $60 \degree$ C) and permeate pressures (10 mbar to 80 mbar). Feed mixtures contained acetone, butanol and ethanol in a 3:6:1 ratio.

Component 1	Water	Water	Water	Water	· Water	Butanol	Butanol	Butanol
Component 2	Butanol	Acetone	Ethanol	Acetic a	ac. Butyric A	Ac. Acetone	Ethanol	Acetic ac.
Source	Regression <sup>a)</sup>	APV72 VLE-IG	APV72 VLE-IG	APV72 VLE-HC	2 APV72 DC VLE-LI	2 APV72 T VLE-LIT	APV72 VLE-LIT	APV72 VLE-HOC
a <sub>12</sub> [-]	4.812	0.0544	3.4578	3.329	0	0	0	0
a <sub>21</sub> [-]	-0.274	6.398	-0.801	-1.976	6 0	0	0	0
b <sub>12</sub> [K]	-295.802	419.971	-586.080	-723.88	38 1176.96	299.218	8.437	-381.596
b <sub>21</sub> [K]	132.137	-1808.991	246.18	609.88	9 14.810	-43.141	33.483	550.162
C <sub>12</sub> [-]	0.3	0.3	0.3	0.3	0.397	0.3	0.347	0.3
Component i	Acetone	Acetone	e Eth	nanol	Acetic ac.	Butanol	Ethanol	Acetone
Component j	Ethanol	Acetic a	c. Ace	tic ac.	Butyric Ac.	Butyric Ac.	Butyric Ac.	Butyric Ac.
Source	APV72 VLE-RK	APV72 VLE-HO	AF C VLE	vV72 -HOC	UNIFAC	UNIFAC	UNIFAC	UNIFAC
a <sub>12</sub> [-]	-1.030	0		0	0.469	-0.287	0.348	0.169
a <sub>21</sub> [-]	-0.259	0	0		-0.408	0.224	-0.163	-0.148
b <sub>12</sub> [K]	416.749	667.699	667.699 22		49.707	-204.316	103.343	675.567

	Table A1: NRTL Binar	y Parameter Sets for	Calculation of Va	pour-Liquid Ec	uilibria with As	pen Properties®
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<sup>a</sup>Regression was necessary to reliably describe activity coefficients of butanol at small concentrations and at infinite dilution. The data used for fitting were taken from:

-252.482

0.3

• Iwakabe K, Kosuge H. Isobaric vapor-liquid-liquid equilibria with a newly developed still. Fluid Phase Equilib 2001; 192, 1-2: 171-186.

-392.710

0.3

 Gao Z, Wang S, Sun Q, Zhang F. Isobaric phase equilibria of the system 1-butanol + water containing penicillin G potassium salt at low pressures. Fluid Phase Equilib 2003; 214, 2: 137-149.

-15.044

0.3

300.426

0.3

-122.242

0.3

-389.848

0.3

 Tikhonov MB, Markuzin NP, Toikka AM. Liquid-vapor equilibrium and open evaporation in dibutyl ether-water-n-butyl alcohol systems. Zh Obshch Khim 1995; 65, 2: 180-184.

Butler JAV, Thompson, DW, MacLennan WH. 173. The free energy of the normal aliphatic alcohols in aqueous solution. J of the Chem Soc 1933: 674-686.

 Kojima K, Zhang S, Hiaki T. Measuring methods of infinite dilution activity coefficients and a database for systems including water. Fluid Phase Equilib 1997; 131, 1-2: 145-179.