

γ -Valerolactone as Bio-Based Solvent for Nanofiltration Membrane Preparation

Muhammad Azam Rasool and Ivo F. J. Vankelecom *

Membrane Technology Group (MTG), Division cMACS, Faculty of Bioscience Engineering, KU Leuven, Celestijnenlaan 200F, P.O. Box 2454, 3001 Leuven, Belgium; ma.rasool@kuleuven.be

* Correspondence: ivo.vankelecom@kuleuven.be; Tel.: +32-16321594

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Hansen solubility parameters

Hansen divided the heat of vaporization energy into 3 different parts and processed as dimensional vectors which are δ_D , δ_P , and δ_H and are attributed to polar forces, dispersive forces, and hydrogen bonding respectively. Hildebrand parameter is a geometric means of HSP parameters and calculated by equation 1 [1]. From table S4, the total solubility values of polymers and GVL have difference in values but still they formed a homogeneous solution, most probably due to size of GVL.

$$\delta_t = \sqrt{\delta_D^2 + \delta_P^2 + \delta_H^2} \quad (1)$$

These three HSPs are modelled as a sphere with radius R and centered at δ_D , δ_P , and δ_H of the polymer is plotted and R_0 is the critical radius of interaction of a polymer.

HSP values for polymers and GVL is given in tables (S1–S5), which were taken from literature. [2–5] Relative energy difference (RED) is equal to R_a/R , used to explain the solubility of polymers in a given solvent by a single parameter [6–8]. Smaller values of R_a represent that they can make a homogeneous solution. A single parameter to describe solvent quality and its ability to dissolve a polymer is RED (relative energy difference), which equals R_a/R .

$$RED = \frac{R_a}{R} \quad (2)$$

While R_a is interaction distance between polymer and solvent, R is the sphere of the solubility radius of the polymer. If the RED value is smaller than 1, this indicates a high affinity

between polymer and solvent, polymer should be soluble in the given solvent. When the RED value is higher than 1, indicates a low affinity between solvent and the polymer and the polymer would probably not be soluble in given solvent. Details of the HSP and RED values are given in each table (Table S1-S5). Solubility parameters difference (Ra) of GVL and non-solvent is given in table S6.

Table S1. Hansen solubility parameters and relative energy difference (RED) for CA.

Polymer/Solvent	δ_D	δ_P	δ_H	δ	R	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
CA	16	7.5	13.5	22.2	8.8	
	Hansen Solubility Parameters				Ra (MPa ^{1/2})	RED = R/R
	δ_D	δ_P	δ_H	δ		
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}		
GVL	15.5	4.7	6.6	17.4	10.5	1.2

Table S2. Hansen solubility parameters and relative energy difference (RED) for PI.

Polymer/Solvent	δ_D	δ_P	δ_H	δ	R	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
PI(Polyimide)	20.9	11.3	9.7	25.7	13.4	
Solvent	Hansen Solubility Parameters				Ra (MPa ^{1/2})	RED = Ra/R
	δ_D	δ_P	δ_H	δ		
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}		
GVL	15.5	4.7	6.6	17.4	13.1	0.9

Table S3. Hansen solubility parameters and relative energy difference (RED) for PSU.

Polymer/Solvent	δ_D	δ_P	δ_H	δ	R	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
PSU	19.7	8.3	8.3	22.9	8	
Solvent	Hansen Solubility Parameters				Ra (MPa ^{1/2})	RED = Ra/R
	δ_D	δ_P	δ_H	δ		
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}		
GVL	15.5	4.68	6.56	17.4	9.4	1.1

Table S4. Hansen solubility parameters for PES and relative energy difference (RED) for PES.

Polymer/Solvent	δ_D	δ_P	δ_H	δ	R	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
PES	19.6	10.8	9.2	24.2	6.2	
Solvent	Hansen Solubility Parameters				Ra (MPa ^{1/2})	RED = Ra/R
	δ_D	δ_P	δ_H	δ		

	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}		
GVL	15.5	4.7	6.6	17.4	10.6	1.7

Table S5. Hildebrand/Hansen solubility parameters of GVL and interaction distance for CTA.

Polymer/Solvent	δ_D	δ_P	δ_H	δ	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
CTA	18.0	12.0	10.0	23.8	
Solvent	Hansen Solubility Parameters				Ra (MPa ^{1/2})
	δ_D	δ_P	δ_H	δ	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
GVL	15.5	4.7	6.6	17.4	9.5

Table S6. Solubility parameters difference (Ra) of GVL and non-solvent.

Solvent/Non-Solvent	δ_D	δ_P	δ_H	δ	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	
Water (as Non-Solvent)	15.5	16	42.3	47.8	
Solvent	Hansen Solubility Parameters				Ra (MPa ^{1/2})
	δ_D	δ_P	δ_H	δ	
	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	

Table S7. Comparison of the overall membranes performance of current membranes and a selection of lab-made and commercial membranes.

Reference/ Membrane ID	Membrane Material		Permeance (L/m ² h ⁻¹ bar ⁻¹)	Rejection (%)		
	Support	Top Layer/Brand-Name		RB	MgSO4	NaCl
Hermans [9]	PSf	PA	2.04 (H2O)	100	96	93
Hermans [10]	XL PI	PA	2.65 (C2H5OH)	100		
Marien[11]	PSf	PA	1.23 (H2O) 0.38 (C2H5OH)	98		96
	XL PI	PA	1.09 (H2O) 0.61 (C2H5OH)	99		97
Dom [12]	XL PI	poly(β -alkanolamine)	1.99 (C2H5OH)	94		
	XL PI	poly(β -alkanolamine)	1.57 (C2H5OH)	100		
	XL PAN	poly(β -alkanolamine)	0.46 (C2H5OH)	99		
	XL PI	poly(epoxyether)	2.18 (C2H5OH)	97		
	XL PI	poly(epoxyether)	1.66 (C2H5OH)	99		
	XL PAN	poly(epoxyether)	0.47 (C2H5OH)	90		

Van Goethem [13]	PSf	PA with ZIF-8	2.70 (H ₂ O)		82
Daem [14]		PVDF-g-PSSA	2.40 (H ₂ O)	99	77
Solomon [15]	XL PI	PA	1.53 (THF)	99	
			1.54 (DMF)	99	
Solomon [16]	XL PI	polyarylate	8.0 (CH ₃ OH)	99	
			3.8 (THF)		
Burgal [17]		PEEK	0.22(THF)		
Karan [18]	alumina	PA	52 (CH ₃ OH)		
	XL PI	PA	19 (CH ₃ OH)		
Evonik [11,19–21]	XL PI	Duramem 150	0.15–0.35 (C ₂ H ₅ OH)		
			0.09 (CH ₃ OH)		
			0.10 (THF)		
			0.16 (C ₂ H ₅ OH)		
		Duramem 200	0.28 (C ₂ H ₅ OH)		
			0.22–0.64		
			0.43 (C ₂ H ₅ OH)		
			NF030306		
		Duramem 300	0.38 (C ₂ H ₅ OH)		
			1.20 (C ₂ H ₅ OH)		
Solsep [22,23]		NF030306	0.38 (C ₂ H ₅ OH)		
		Solsep3360	1.20 (C ₂ H ₅ OH)		
Dow [24] [25]		PA- NF90	6.67 (H ₂ O)		
			8.54 (H ₂ O)	>97	85–95
			10.38 (H ₂ O)		
		PA (PIP)- NF270	11.04 (H ₂ O)	>96	82
Hydranautics [24,26,27]	PA	ESNA	4.90 (H ₂ O)		
			4.38 (H ₂ O)		70
Yoon [26]	PA	LFC-1 (RO)	3.13 (H ₂ O)		
Koch [24,28]		TFC-S	3.68 (H ₂ O)		
			11.00 (H ₂ O)		85
Toray [28]		UTC-20			
		TMG-10PA (PIP)	9.17 (H ₂ O)		99
GE osmonics [29]		desal-DK	4.43 (H ₂ O)		
			1.13 (C ₂ H ₅ OH)	> 98	
		AD-90	0.51 (H ₂ O)		>99
		AG2540FM	2.79 (H ₂ O)		>99
Rasool [7]	C15	CA	12.8 (H ₂ O)	92.9	80.2
	C17.5	CA	5.7 (H ₂ O)	98.1	80.9
	C20	CA	2.4 (H ₂ O)	99.5	82.5
	C10/10	CA	3.5 (H ₂ O)	92.8	
	C10/30	CA	1.3 (H ₂ O)	91.8	
	C10/10E	CA	3.5 (H ₂ O)	94.3	
	C10/30E	CA	1.3 (H ₂ O)	90.6	

Current membranes	C20/10E	CA	1.1 (H ₂ O)	99.7	96.5
	C20/30E	CA	0.7 (H ₂ O)	99.5	71.5
	C20/50E	CA	0.2 (H ₂ O)	98.8	63.9
	C20/10	CA	1.0 (H ₂ O)	99.8	92.9
	C20/30	CA	0.7 (H ₂ O)	99.7	79.9
	C20/50	CA	0.2 (H ₂ O)	98.9	81.3
	CA15E	CA	1.9 (H ₂ O)	96.2	
	CTA10W	CTA	20.1 (H ₂ O)	94.0	
	CTA15W	CTA	16.8 (H ₂ O)	94.3	
	CTA17.5W	CTA	12.2 (H ₂ O)	98.8	
	PES15E	PES	2.6 (H ₂ O)	96.2	
	PES20E	PES	1.1 (H ₂ O)	96.4	
	PSU15E	PSU	2.2 (H ₂ O)	92.1	
	PSU20E	PSU	0.7(H ₂ O)	98.5	
	PI15E	PI	2.5(H ₂ O)	98.7	
	PI20E	PI	0.8 (H ₂ O)	98.7	

Table S8. Comparison of the overall membranes performance of current membranes and a selection of lab-made and commercial membranes using MgSO₄ feed solution.

Manufacturer	Type	Polymer	MgSO ₄ Rejection (%)	Permeance (L/m ² h ⁻¹ bar ⁻¹)
Dow Filmtec™	NF270	Polyamide-TFC	99.2	16.3
	NF90	Polyamide-TFC	99.0	9.5
	NF	Polyamide-TFC	99.0	6.1
GE Osmonics™	Duracid	Polyamide-TFC	98.0	1.6
	DL	Polyamide-TFC	98.0	3.1
	HL	Polyamide-TFC	98.0	9.7
	DK	Polyamide-TFC	96.0	5.4
	CK	Cellulose Acetate	94.0	3.4
Synder™	NFX	Polyamide-TFC	99.0	4.9
	NFW	Polyamide-TFC	97.0	10.2
	NFG	Polyamide-TFC	50.0	13.6
	NDX	Polyamide-TFC	90.0	12.4
	TS80	Polyamide-TFC	99.0	4.5
TriSep™	SB90	Cellulose Acetate Blend	97.0	3.3
	SBNF	Cellulose Acetate	60.0	2.1
	TS40	Polypiperazine-amide-TFC	90.0	4.5
	XN45	Polypiperazine-amide-TFC	95.0	7.9
Microdyn Nadir™	NP010	PES	60.0	5.0
	NP030	PES	60.0	1.0
S. W. Lin et al		AV-NF-Pip 1	92.5	9.0

[5]	AV-NF-Pip 2	96.1	12.0
	AV-NF-Pip 3	97.4	9.4
	AV-NF-Pip 4	96.4	10.3
	AV-PVA-1	98.0	11.7
	AV-PVA-2	97.8	9.4
	AV-PVA-3	97.7	8.7
	AV-PVA-4	96.5	8.5
	AV-NF-TMC 1	97.3	9.4
	AV-NF-TMC 2	98.2	12.0
	AV-NF-TMC 3	97.6	13.0
Rasool et al [7]	CA15	80.2	12.6
	CA17.5	80.9	5.6
	CA20	82.4	2.4
	CA20/0	80.1	3.8
	CA20/10	92.1	1.0
	CA20/30	79.9	0.7
	CA20/50	81.3	0.2
	CA20/10E	96.5	1.1
	CA20/30E	72.5	0.6
	CA20/50E	70.9	0.2
	CA20W	63.2	0.6
	CTA10W	18.5	20.1
	CTA15W	25.1	16.8
	CTA17.5W	25.5	12.2
	PES15E	49.2	2.6
	PES20E	68.1	1.1
	PSU15E	12.5	2.2
	PSU15E	54.1	0.7
	PI15E	14.5	2.6
	PI20E	18.3	0.8

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