Electronic Supporting Information

Unleashing the potential of castor oil as extraction solvent of carotenoids from tomatoes

Bárbara M.C. Vaz,[1#] Letícia S. Contieri,[1,2#] Filipe H.B. Sosa,[1] Margarida Martins,[1] Alexandra Conde,[1] Ana C.R.V. Dias,[3] Maurício A. Rostagno,[2] Leonardo M. de Souza Mesquita,[2*] Sónia P.M. Ventura[1*]

[1]CICECO − Aveiro Institute of Materials, Department of Chemistry, University of Aveiro Campus Universitário de Santiago, 3810-193 Aveiro, Portugal.

[2]Multidisciplinary Laboratory of Food and Health (LabMAS), School of Applied Sciences (FCA), University of Campinas, Rua Pedro Zaccaria 1300, 13484-350, Limeira, São Paulo, Brazil.

[3]CESAM - Centre for Environmental and Marine Studies, Department of Environment and Planning, University of Aveiro, 3810-193 Aveiro, Portugal.

Both authors worked equally on this manuscript.

*Corresponding authors

Sónia P.M. Ventura: spventura@ua.pt. OCID ID: 0000-0001-9049-4267

Leonardo M. de Souza Mesquita: mesquitalms@gmail.com. ORCID ID: 0000-0002-7602-7731

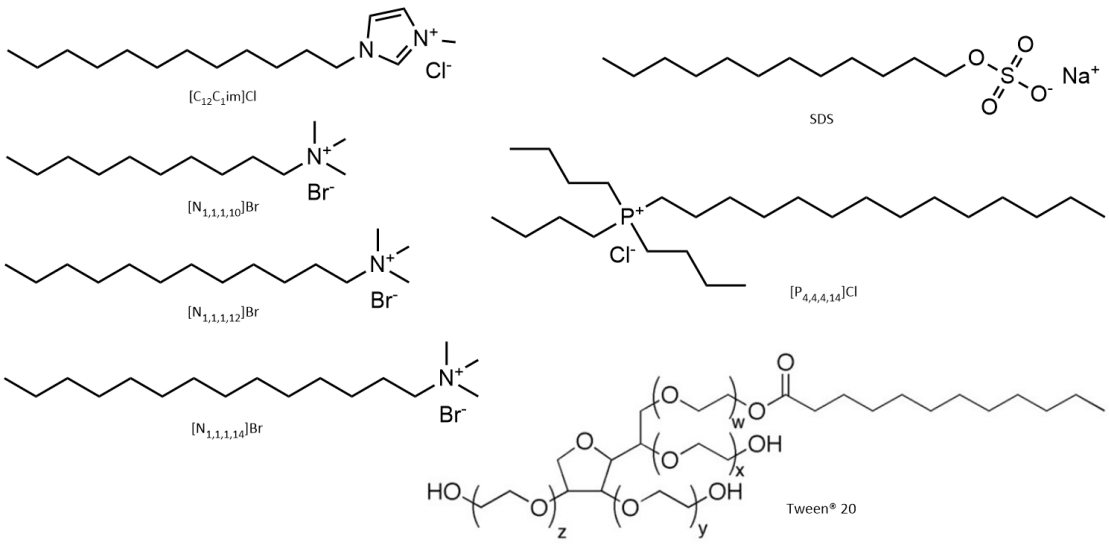

Figure S1. Molecular structure and respective abbreviation of the ILs/surfactants screened in this work.

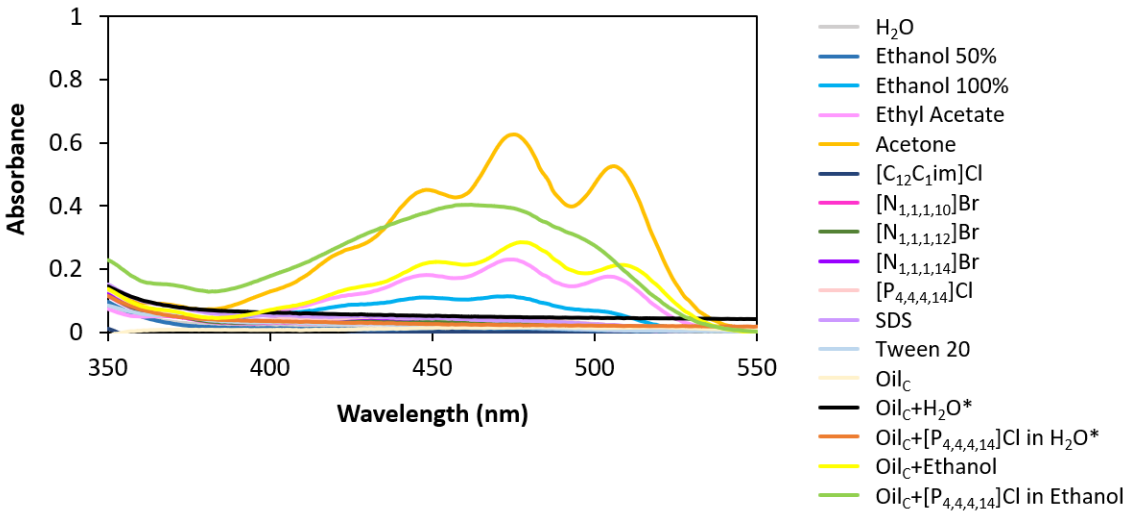

Figure S2. UV-Vis spectroscopy of the extracts obtained in the initial screening of this work. *Systems with two phases, where these results are related to the bottom phase composed of water.

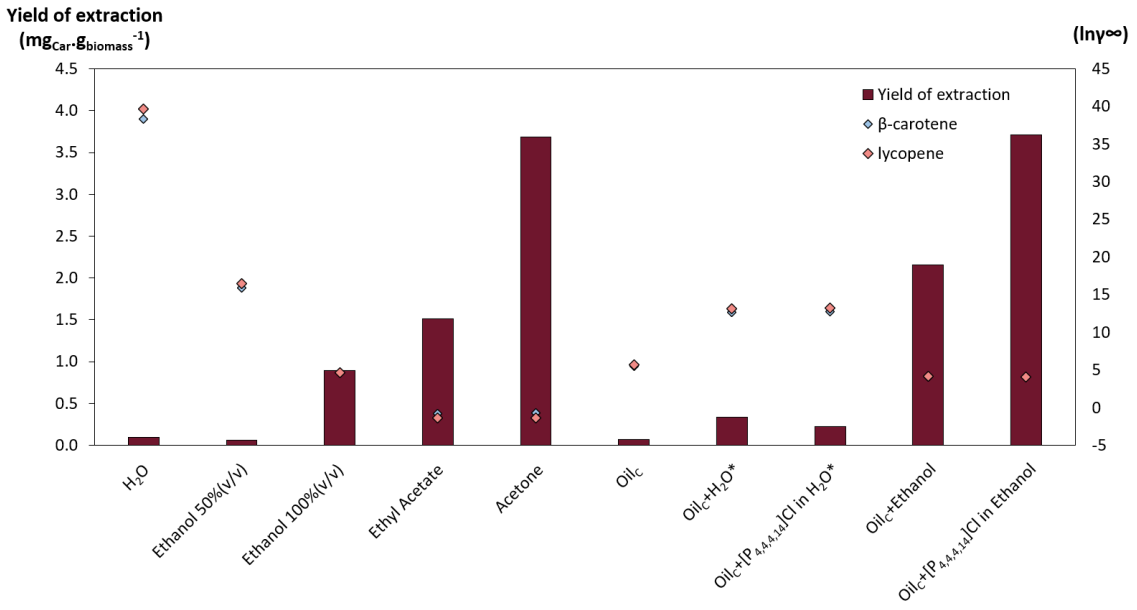

Figure S3. Yield of extraction and the activity coefficients at infinite dilution (lnγ∞) of β-carotene and lycopene, using distilled water, organic solvents, and castor oil mixtures with 16%(v/v) of Oil$_C$. *systems with two phases, where these results are related to the bottom phase composed of water.

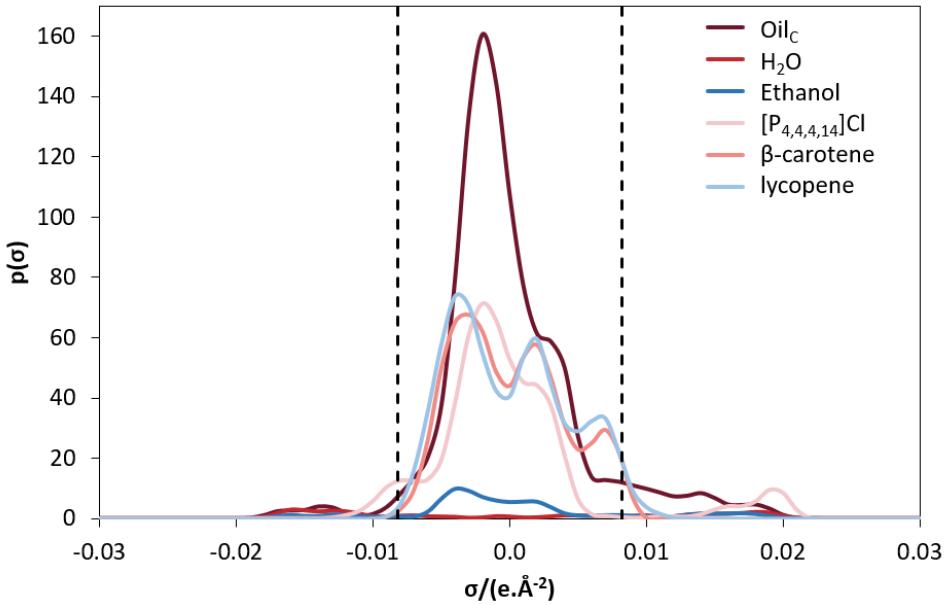

Figure S4. σ-Profiles of castor oil (Oil$_C$), water (H$_2$O), ethanol, [P$_{4,4,4,14}$]Cl, β-carotene, and lycopene.

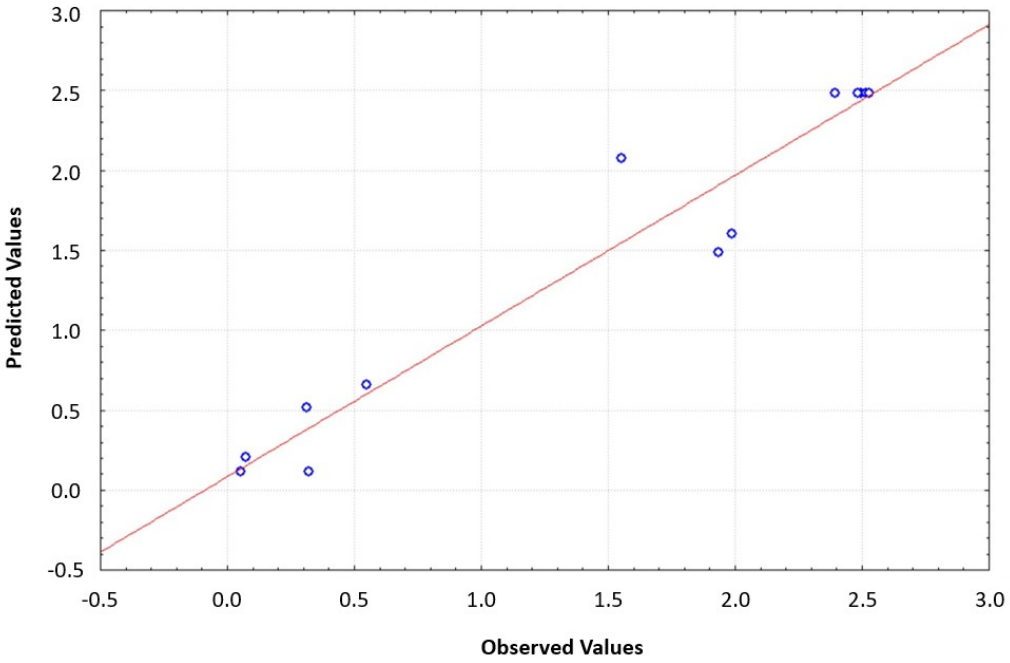

Figure S5. Predicted *vs.* experimental values of the CCRD (2^2) regarding carotenoids yield of extraction ($mg_{Car}.g_{biomass}^{-1}$) using an Oil_C + Ethanol system.

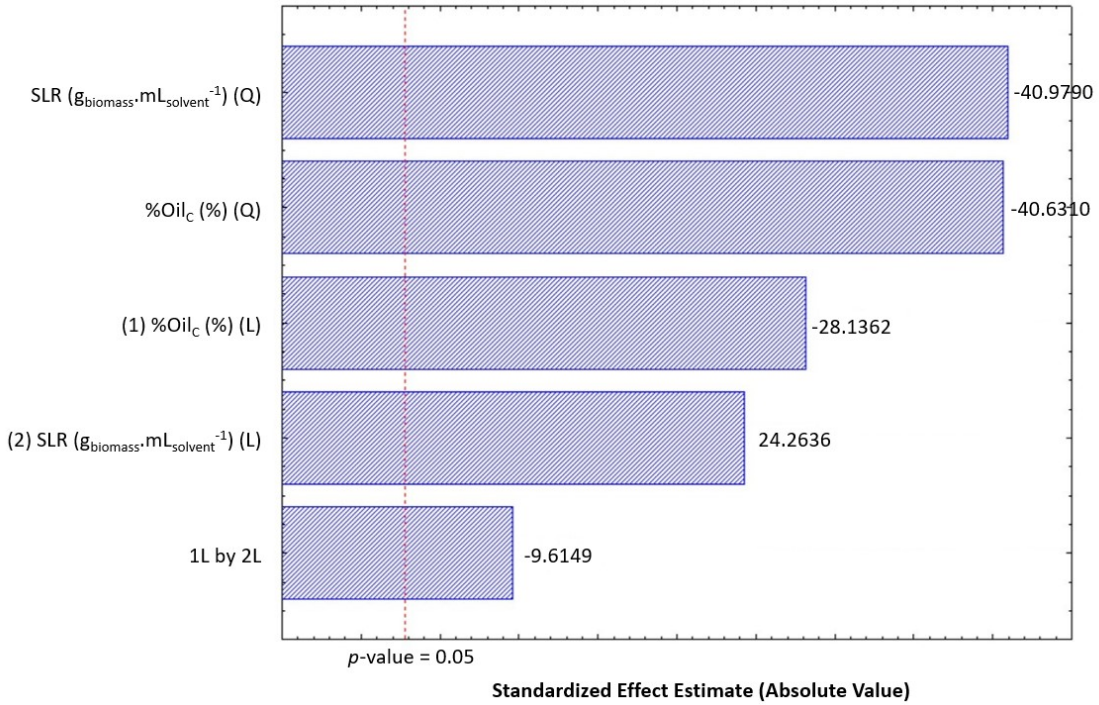

Figure S6. Pareto Chart of the CCRD (2^2) regarding carotenoids yield of extraction ($mg_{Car}.g_{biomass}^{-1}$) using an Oil_C + Ethanol system.

Table S1. Critical Micellar Concentration (CMC) of surface-active compounds used in the initial screening of this work.

Surface-active compound	CMC (mM)	Reference
$[C_{12}C_1im]Cl$	15	[1]
$[N_{1,1,1,10}]Br$	25.2	[2]
$[N_{1,1,1,12}]Br$	14	[3]
$[N_{1,1,1,14}]Br$	3.6	[4]
$[P_{4,4,4,14}]Cl$	4.69	[2]
SDS	8	[5]
Tween® 20	0.078	[5]

Table S2. Real and encoded values used in the optimization process by CCRD (2^2) expressed by carotenoids yield of extraction ($mg_{Car}.g_{biomass}^{-1}$). For all assays the total volume of the system Oil_C + Ethanol was kept constant at 5 mL.

Run	$\%Oil_C$ (%)	SLR ($g_{biomass}.mL_{solvent}^{-1}$)	Yield of extraction ($mg_{Car}.g_{biomass}^{-1}$)
1	25.0 (-1)	0.020 (-1)	0.55
2	75.0 (1)	0.020 (-1)	0.32
3	25.0 (-1)	0.100 (1)	1.55
4	75.0 (1)	0.100 (1)	0.31
5	14.8 (-1.41)	0.060 (0)	1.99
6	85.3 (1.41)	0.060 (0)	0.05
7	50.0 (0)	0.004 (-1.41)	0.07
8	50.0 (0)	0.116 (1.41)	1.94
9	50.0 (0)	0.060 (0)	2.50
10	50.0 (0)	0.060 (0)	2.39
11	50.0 (0)	0.060 (0)	2.52
12	50.0 (0)	0.060 (0)	2.53
13	50.0 (0)	0.060 (0)	2.48

Table S3. Inventory data for the calculation of the carbon footprint.

Parameter	Unit	Amount
Inputs		
Tomatoes	kg	1.00
Ethanol	L	6.25
Castor oil	L	6.25
Electricity - grinding	kWh	0.22
Electricity - extraction	kWh	7.50
Electricity - centrifugation	kWh	29.17
Electricity - rotative evaporator	kWh	4.58
Outputs		
By-products - skins, seeds and used tomato pulp	kg	1.00

Table S4. List of solvent functions used during the initial screening for their application in cosmetic formulations, referencing data sourced from the European Commission database [6].

Compound	Function(s)
Water	Solvent
Ethanol	Antifoaming Antimicrobial Astringent Fragrance Solvent Viscosity controlling
Acetone	Denaturant Fragrance Solvent
Ethyl Acetate	Perfuming Solvent
$[C_{12}C_1im]Cl$	-
$[N_{1,1,1,10}]Br$	-
$[N_{1,1,1,12}]Br$	Hair conditioning Preservative
$[N_{1,1,1,14}]Br$	Preservative

$[P_{4,4,4,14}]Cl$	-
SDS	Cleansing Denaturant Foaming
Tween® 20	Emulsifying Cleansing
Castor Oil	Fragrance Skin conditioning Perfuming

Table S5. Effect of the estimates for carotenoids yield of extraction ($mg_{Car}.g_{biomass}^{-1}$) using an Oil_C + Ethanol system optimized by the CCRD (2^2). Significant factors are presented at a 95% confidence level.

Factor	**Effect**	**Standard error**	**Calculated *t*** *	***p*-value**
Mean/Interaction	2.48	0.02	105.12	0.000
$\%Oil_C$ (%) - (X1)	-1.05	0.04	-28.14	0.000
$\%Oil_C$ (%) - ($X1^2$)	-1.64	0.04	-40.63	0.000
SLR ($g_{biomass}.mL_{solvent}^{-1}$) - (X2)	0.91	0.04	24.26	0.000
SLR ($g_{biomass}.mL_{solvent}^{-1}$) - ($X2^2$)	-1.65	0.04	-40.98	0.000
1L by 2L	-0.51	0.05	-9.61	0.001

Table S6. Predicted *vs.* experimental values (real) obtained by the fitted model and the respective relative deviation (%) from the independent variables fixed at the optimum operational conditions. V1, V2, and V3 represent the validation assays.

Assay	%Oil_C (%)	SLR ($g_{biomass}.mL_{solvent}^{-1}$)	Yield of extraction ($mg_{Car}.g_{biomass}^{-1}$) using an Oil_C + Ethanol system		Relative deviation (%)
			Experimental values	Predicted values	
	X1	X2	Y	Predicted Y	
V1	50	0.06	2.99	3.26	8.04
V2			3.30		1.23
V3			2.63		19.2
				Mean of deviation	9.48

References

[1] M. Blesic, M.H. Marques, N. V. Plechkova, K.R. Seddon, L.P.N. Rebelo, A. Lopes, Self-aggregation of ionic liquids: micelle formation in aqueous solution, Green Chem. 9 (2007) 481–490. https://doi.org/10.1039/b615406a.

[2] F.A. Vicente, I.S. Cardoso, T.E. Sintra, J. Lemus, E.F. Marques, S.P.M. Ventura, J.A.P. Coutinho, Impact of Surface Active Ionic Liquids on the Cloud Points of Nonionic Surfactants and the Formation of Aqueous Micellar Two-Phase Systems, J. Phys. Chem. B. 121 (2017) 8742–8755. https://doi.org/10.1021/acs.jpcb.7b02972.

[3] M.A. Bahri, M. Hoebeke, A. Grammenos, L. Delanaye, N. Vandewalle, A. Seret, Investigation of SDS, DTAB and CTAB micelle microviscosities by electron spin resonance, Colloids Surfaces A Physicochem. Eng. Asp. 290 (2006) 206–212. https://doi.org/10.1016/j.colsurfa.2006.05.021.

[4] S.P. Moulik, M.E. Haque, P.K. Jana, A.R. Das, Micellar Properties of Cationic Surfactants in Pure and Mixed States, J. Phys. Chem. 100 (1996) 701–708. https://doi.org/10.1021/jp9506494.

[5] Y. Shi, H.Q. Luo, N.B. Li, Determination of the critical premicelle concentration, first critical micelle concentration and second critical micelle concentration of surfactants by resonance Rayleigh scattering method without any probe, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 78 (2011) 1403–1407. https://doi.org/10.1016/j.saa.2011.01.018.

[6] E. Commission, CosIng - Cosmetics Ingredients, (n.d.). https://ec.europa.eu/growth/tools-databases/cosing/ (accessed August 24, 2023).