

Supplementary Material
Estimation of Reactivity Ratios for Olefin Polymerization Catalysts – On the
importance of thermodynamics

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S1. Calculation of the Joint Confidence Intervals

In this present work, the global reactivity ratios will be estimated by considering both the confidence interval (CI) and joint confidence region (JCR). The confidence interval for the reactivity ratios is expressed as[1]:

$$r_i \pm t_{\alpha/2, d-p} \sqrt{s (J'J)_{ii}^{-1}} \quad 5.18$$

where the number of data points and parameters are respectively represented by d and p . The upper $100 \times \alpha/2$ percentage point of the t -distribution with $d - p$ degrees of freedom is denoted by $t_{\alpha/2, d-p}$. [1] J is the Jacobian matrix evaluated at the optimum parameter values and is expressed as

$$J = \left[\frac{\partial g(f_E, r)}{\partial (r_j)} \right] (i, j) \text{th element} \quad 5.19$$

the parameter r_j has a function g as its coefficient and $(J'J)_{ii}^{-1}$ is the i th diagonal element of matrix $(X'X)$. The parameter s can be evaluated with the expression.

$$s^2 = \frac{S(\hat{r})}{d-p} \quad 5.20$$

The sum of square computed at the optimum value of the parameters is denoted as $S(\hat{r})$. Confidence interval is an asymptotic estimator of r_E and r_H which can lead to insufficient information about the statistics involved [2]. A more precise and detailed way of computing the uncertainty in parameter estimation is through JCR which is a multi-dimensional

generalization of CI. The JCR involve all combinations of estimated values for the parameters at a particular confidence level. In this present study, the JCR for estimating reactivity ratio can be pictured as an error ellipse. The assumption made is that the error is distributed normally with a known variance. The expression below describes joint posterior probability region for parameter estimation.

$$(r - \check{r})J(r - \check{r}) \leq \chi_{(p,0.95)}^2 \quad 5.21$$

where \check{r} denotes estimates of the reactivity ratio r , J is the Jacobian matrix of the estimated r and $\chi_{(p,0.95)}^2$ is the value of the chi-squared distribution with p degrees of freedom, exceeded with probability 0.05.

S2. Solubility measurements and parameter estimation.

S2.1 Materials

Argon, hydrogen, ethylene (C2), propane (C3), 1-butene (1-C4), isobutane (iC4) all with a minimum purity of 99.5%, were procured from Air Liquide (Paris, France). Purification columns of zeolite and active carbon were used to purify ethylene before being use. 1-hexene (1-C6) and n-pentane (nC5) with a minimum purity of 99%, was obtained from Sigma-Aldrich ICN (Germany) and was purified through distillation over CaH₂. The co-catalyst (Triethylaluminium) was obtained from Witco (Germany). Two commercial Zeigler-Natta catalysts were used during this work, catalyst 1 was used for the C2 – 1-C6 copolymerization and the C2 – 1-C4 copolymerizations, with and without iC4. Catalyst 2 was used for the other runs. LLDPE powders for the sorption measurements were graciously supplied by Ineos. It has a density of 926 kg/m³ and the crystallinity was found to be 38 weight per cent at 70°C (temperature of the solubility measurements). [3]

S2.1 Pressure Decay Experiments

The sorption experiments carried out using the pressure decay method and apparatus described by Ben M'Rad et al. [3], as was the procedure for identifying the interaction parameters for the SL-EoS. The different vapour mixtures considered in this work, as well as the temperatures, pressure ranges, and compositions are given in Table S1.

Table S1. Temperatures, pressure range and compositions of vapour phase mixtures used in solubility experiments.

System	T (°C)	P (bar)	Composition (Mol fraction)
C2	70	[3.9, 7.2]	
	80	[4.0, 7.4]	
C3	70	[3.5, 4.5]	
	80	[3.5, 4.8]	
1-C4	70	[0.9, 2]	
	80	[0.9, 2.1]	
C2/C3	70	[4.9, 6.8]	$x_{C2} = 0.49, x_{C3} = 0.51$
	80	[5.1, 7.2]	$x_{C2} = 0.50, x_{C3} = 0.49$
C2/1-C4	70	[2.8, 4.1]	$x_{C2} = 0.62, x_{1-C4} = 0.38$
	80	[2.8, 3.8]	$x_{C2} = 0.56, x_{1-C4} = 0.44$
C2/nC5	70	[3.0, 4.1]	$x_{C2} = 0.87, x_{nC5} = 0.13$
	80	[3.1, 4.8]	$x_{C2} = 0.82, x_{nC5} = 0.18$
C2/C3/1-C4	70	[2.6, 4.1]	$x_{C2} = 0.31, x_{C3} = 0.33, x_{1-C4} = 0.36$
	80	[2.7, 4.0]	$x_{C2} = 0.38, x_{iC4} = 0.30, x_{1-C4} = 0.32$
C2/iC4/1-C4	70	[3.1, 4.8]	$x_{C2} = 0.43, x_{iC4} = 0.32, x_{1-C4} = 0.25$
C2/iC5/1-C4	70	[3.0, 4.1]	$x_{C2} = 0.64, x_{iC5} = 0.09, x_{1-C4} = 0.27$
	80	[3.2, 4.3]	$x_{C2} = 0.64, x_{iC5} = 0.10, x_{1-C4} = 0.26$
C2/nC5/1-C4	70	[3.1, 4.7]	$x_{C2} = 0.74, x_{nC5} = 0.08, x_{1-C4} = 0.18$
	80	[3.7, 5.0]	$x_{C2} = 0.69, x_{nC5} = 0.11, x_{1-C4} = 0.20$

The schema for the set-up which is based on pressure decay technique is shown in Figure S1. The reactor equipped with pressure and temperature sensor, a vacuum pump and a recording computer. The reactor is heated by an oil circulating through an external jacket. The ballast in which all component is fed is heated to avoid liquefaction for components heavier than propane. For the liquid alkanes such as n-pentane and iso-pentane, an automated syringe pump was employed to feed the liquid into the ballast. A gas phase chromatograph (microGC agilent 490-Mobile Micro GC, SRA instruments) attached to the connected to the main vessel was employed to measure the composition of the gas phase mixture fed into the reactor. The

MicroGC is connected to the main vessel through a pressure regulating valve. The calibration of the MicroGC was done for each of the studied components. In order to have confidence in the generated data, the MicroGC is calibrated up to a minimum of 8 points. The measurement of the gas phase composition is carried out by injecting the components mixture through a column for period up to 30s. At the beginning and at the end each pressure step, injection into the MicroGC is performed. To main stable gas phase pressure and composition, no further injection id performed during the solubility experiment. The data were acquired and analyzed using SOPRANE II. Analysis and estimation of the interaction parameters for the different systems were performed exactly as described in reference [3]. The binary, ternary and quaternary SL-EoS models can be found in the same reference, and Table S2 shows the parameters of SL EoS for each pure component.

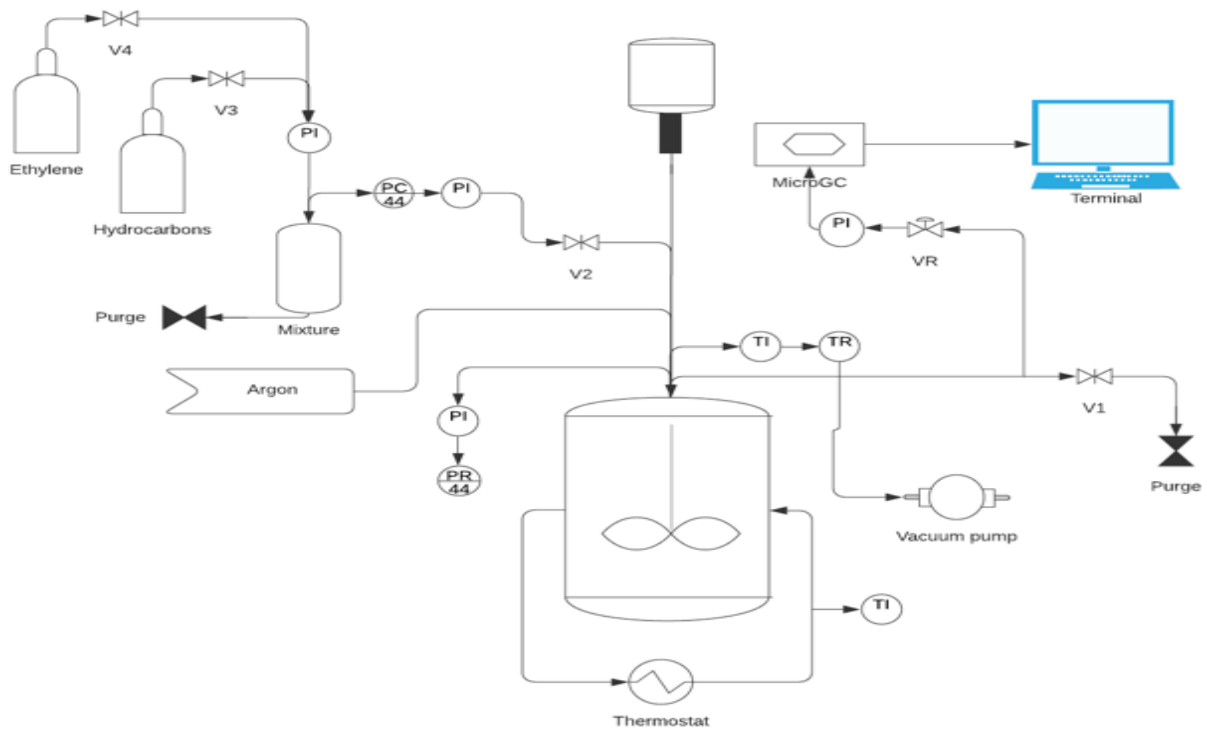


Figure S1. Schema of the pressure decay method experimental set-up.

Table S2: Pure component parameters

Component	$T^*(K)$	$P^*(bar)$	$\rho^*(\frac{kg}{m^3})$	Ref
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Ethylene	283	3395	680	[4]
Propane	371	3090	690	[5]
1-butene	410	3252	814	[6]
isobutane	398	2840	720	[5]
isopentane	424	3040	765	[5]
n-pentane	441	3100	755	[5]
LLDPE	653	4360	903	[4]

S2.3 Solubility results

S2.3.1 Binary systems

Different binary (single penetrant) systems containing ethylene (C2)/LLDPE, propane(C3)/LLDPE, 1-butene (1-C4)/LLDPE, *iso*-pentane (iC5) or *n*-pentane (nC5)/LLDPE were studied. The same LLDPE was used in all experiments. Table S1 shows the range of pressure and temperature of the binary systems investigated. The solubility experiment was performed at a pressure up to 7.2 bar and at a temperature of 70 and 80 °C.

Figure S2 shows the experimental solubility for the studied binary systems. As expected, the individual solubility increases with partial pressure of the system. Table S3 shows the values of the interaction parameters for the temperature range studied.

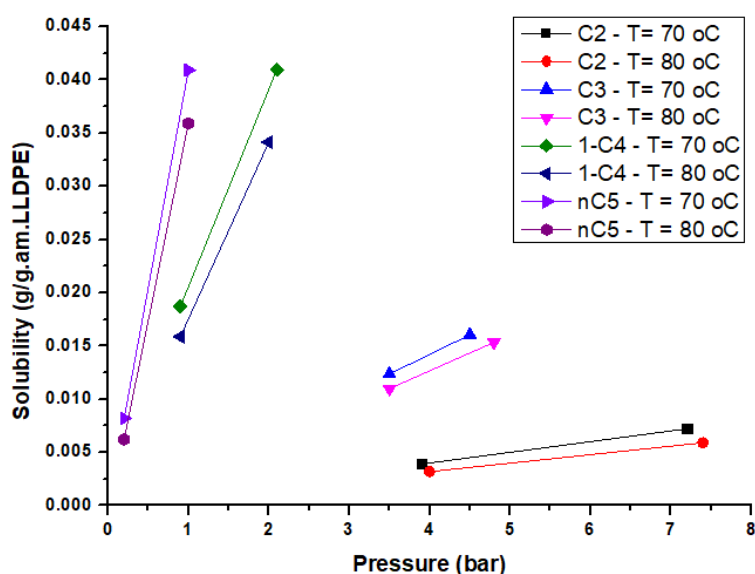


Figure S2. Solubility of pure species in LLDPE at 70° and 80 °C.

Table S3. Interaction parameters for the studied binary system.

System	k_{ij}	
	70 °C	80 °C
Ethylene/LLDPE	-0.01796	-0.0085
Propane/LLDPE	0.0258	0.0227
1-butene/LLDPE	-0.0019	-0.0071
n-pentane/LLDPE	0.0171	0.0139

S2.3.2 Ternary systems

A ternary system is defined as the one containing two penetrants (species 1 is always ethylene, and species 2 can be a comonomer or ICA) and LLDPE (species 3).

Figure S3 compares the total solubility of the three studied ternary systems at total pressures up to 7.2 bar and temperatures of 70° and 80°C. From the figure, it is obvious that the total solubility increases as the total pressure of the system increases. There is also decrease in the solubility as the temperature of the system increases. It is also observed that at a given temperature and total pressure, the heavier the penetrant is, the higher the overall solubility for a given ternary system. Hence, at the same total pressure and temperature of the system, the total solubility is higher in the presence of n-pentane than other components present.

Figure S4a-f shows the total and partial solubilities of the different penetrant in the amorphous phase of the LLDPE at different temperature for each of the ternary systems. The experimental solubility was employed to fit the SL-EoS interaction parameters, k_{ij} , for each system at temperature of 70 and 80 °C. Table S4 shows the k_{ij} values for the temperature range studied here.

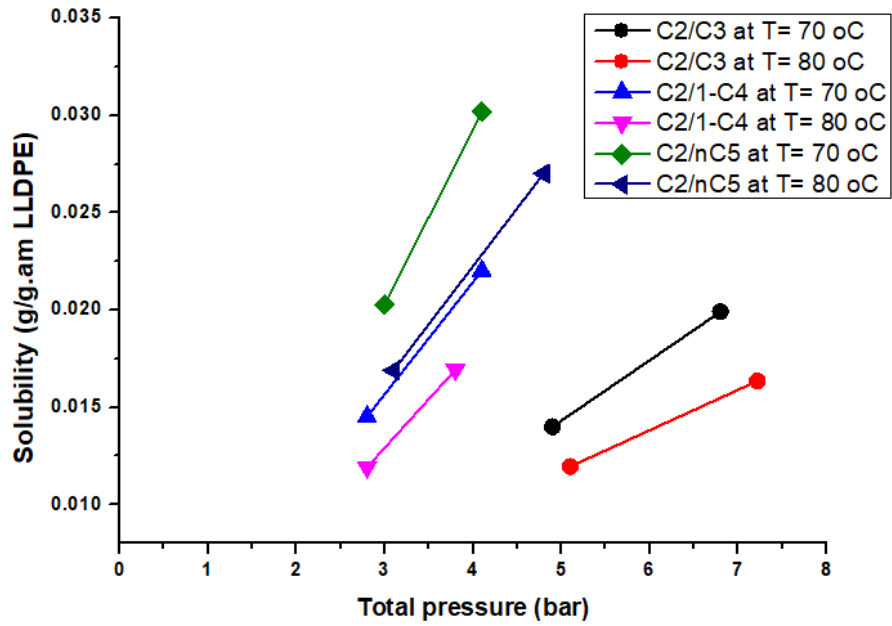
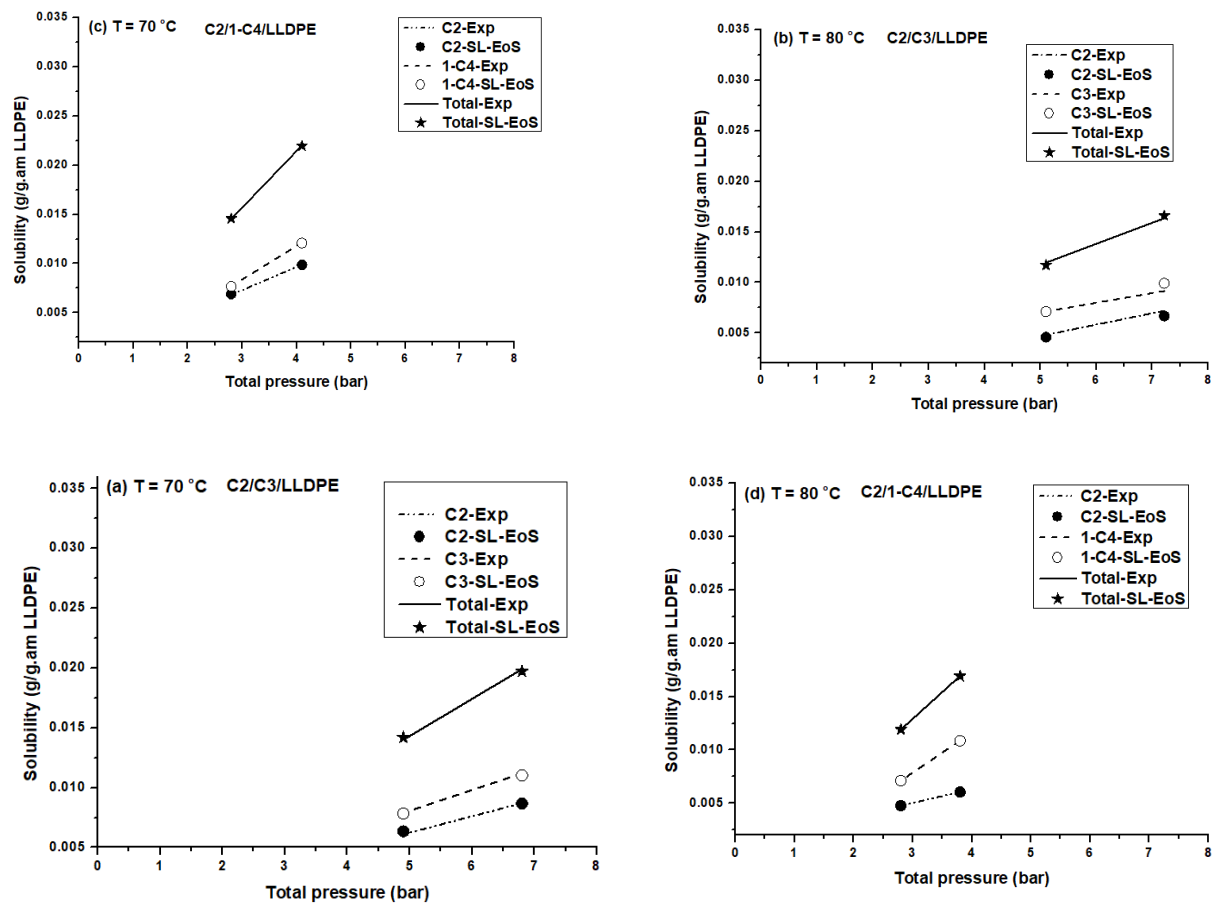


Figure S3: Overall solubility of the studied ternary systems at temperature of 70 and 80 °C. The points denote experimental data while the lines guide the eye only.



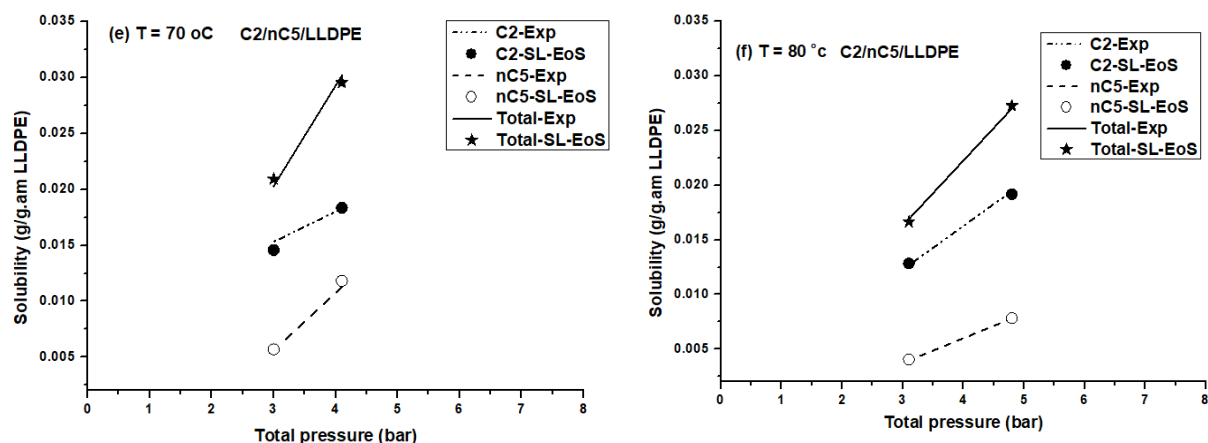


Figure S4. Overall and individual solubilities in the amorphous of the LLDPE for the studied ternary systems at temperature of 70 and 80 °C.

Table S4: Interaction parameter correlation for the studied ternary as a function of temperature

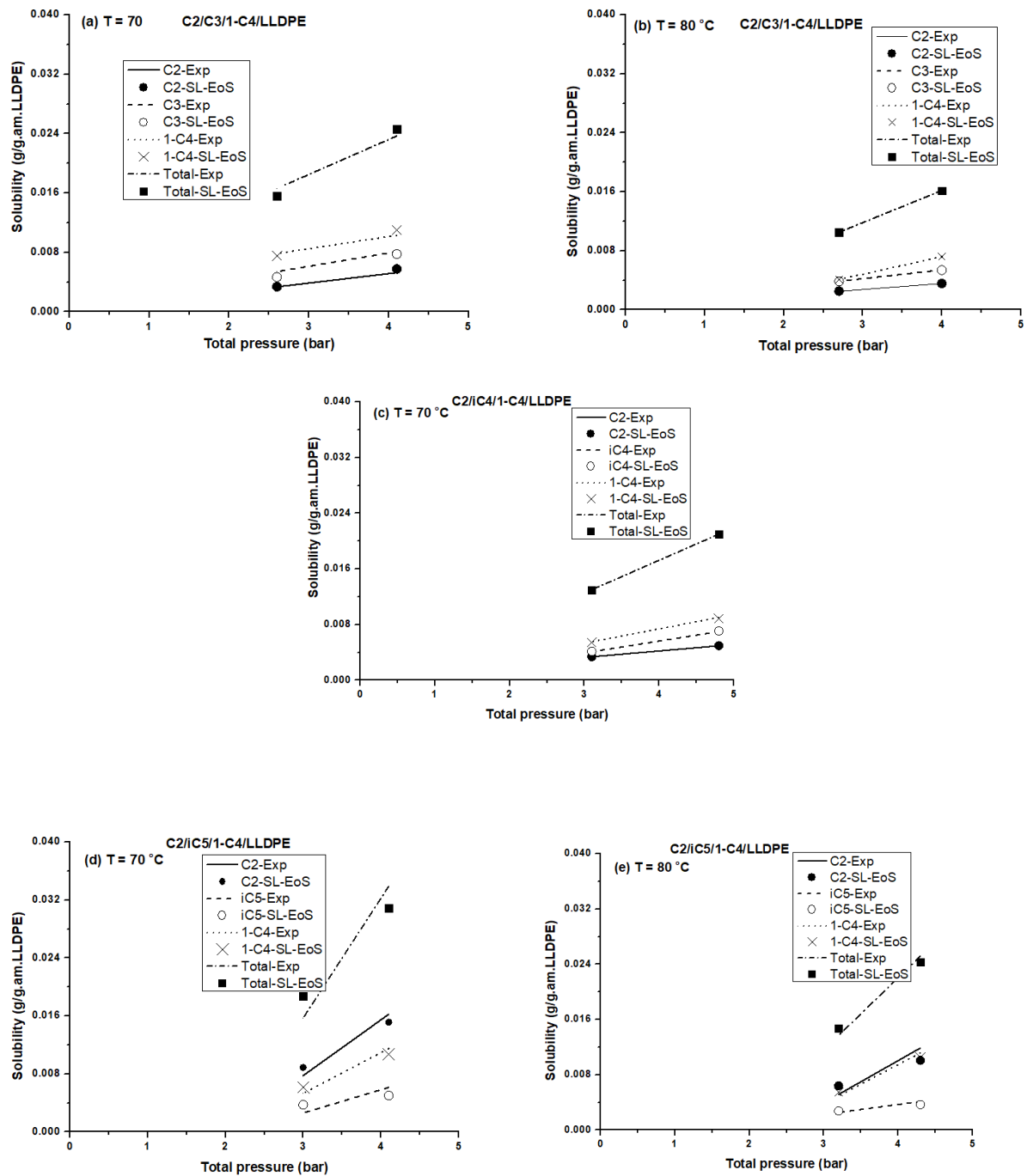
System	k_{ij}	
	70	80
C2/C3/LLDPE	$k_{13} = -0.10136$ $k_{23} = 0.0345$	$k_{13} = -0.0849$ $k_{23} = 0.0335$
C2/1-C4/LLDPE	$k_{13} = -0.1401$ $k_{23} = 0.0508$	$k_{13} = -0.1302$ $k_{13} = -0.0501$
C2/nC5/LLDPE	$k_{13} = -0.1810$ $k_{13} = 0.0760$	$k_{13} = 0.1831$ $k_{13} = 0.081$

S2.3.2 Quaternary systems

The quaternary systems in this present are composed of ethylene (2), ICA (2), comonomer (3) and LLDPE (4). The studied temperatures, pressures and the gas phase molar composition of the different quaternary system studied are displayed in Table S1. The estimated interaction parameters will only be k_{14}, k_{24}, k_{34} as we assume no interaction exist between small olefin, k_{12}, k_{13}, k_{23} . Hence the values are set to zero.

Figures S5(a)-(h) show the overall and partial solubilities of ethylene/propane/1-butene, ethylene/isopentane/1-butene and ethylene/n-pentane/1-butene mixture in LLDPE at 70 and 80°C and that of ethylene/isobutane/1-butene at 70 °C. at total pressure up to 5 bars. The

experimental solubility was employed to fit the SL-EoS interaction parameters, k_{ij} , for each system at temperature of 70 and 80 °C. Table S5 shows the k_{ij} for the quaternary systems.



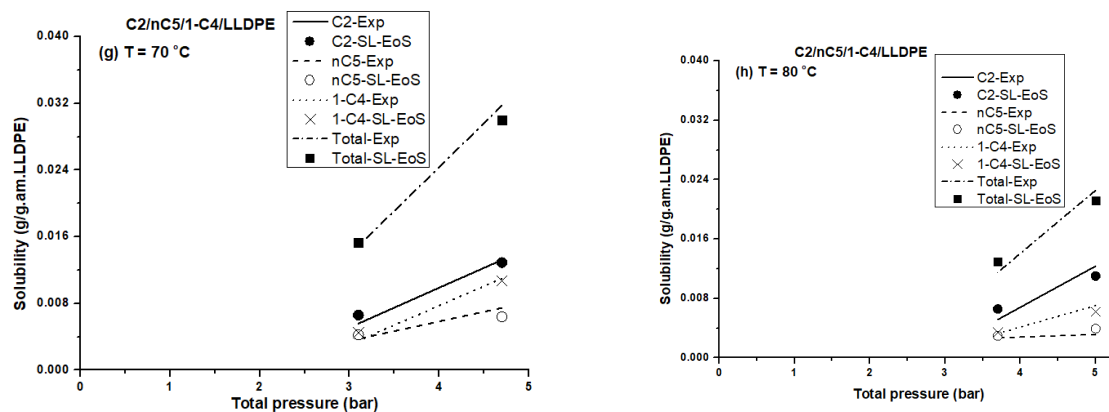


Figure S5: Overall and individual solubilities in the amorphous of the LLDPE for the studied quaternary systems at temperature of 70 and 80 °C.

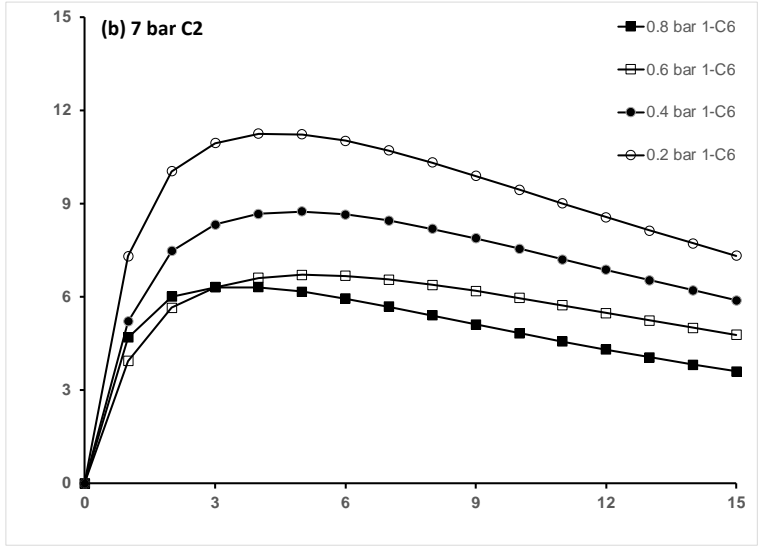
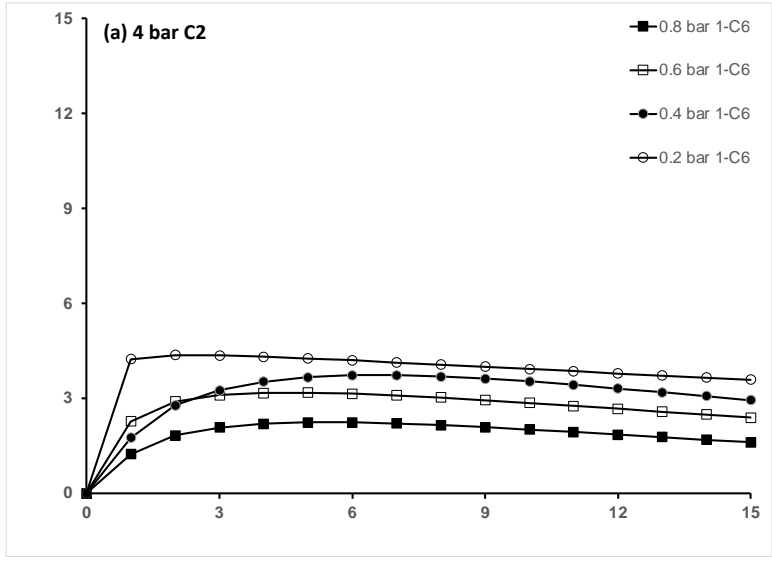
Table S5: Interaction parameters and correlation with temperature for the studied quaternary systems.

System	k_{ij}	
	70	80
C2/C3/1-C4/LLDPE	$k_{14} = -0.1414$ $k_{24} = -0.1034$ $k_{34} = 0.0484$	$k_{14} = -0.1014$ $k_{24} = -0.0053$ $k_{34} = 0.0584$
C2/iC4/1-C4/LLDPE	$k_{14} = -0.0959$ $k_{24} = 0.0443$ $k_{34} = 0.0663$	
C2/iC5/1-C4/LLDPE	$k_{14} = -0.4218$ $k_{24} = 0.1490$ $k_{34} = -0.1304$	$k_{14} = -0.4127$ $k_{24} = 0.1603$ $k_{34} = 0.1323$
C2/nC5/1-C4/LLDPE	$k_{14} = -0.3719$ $k_{24} = 0.1595$ $k_{34} = -0.1128$	$k_{14} = -0.3682$ $k_{24} = 0.1769$ $k_{34} = -0.1003$

S3. Reaction Rates

S3.1 Ternary Systems

The rate profiles for the ethylene co-1-hexene system are shown in Figure S6, and for the ethylene co-1-butene system in Figure S7..



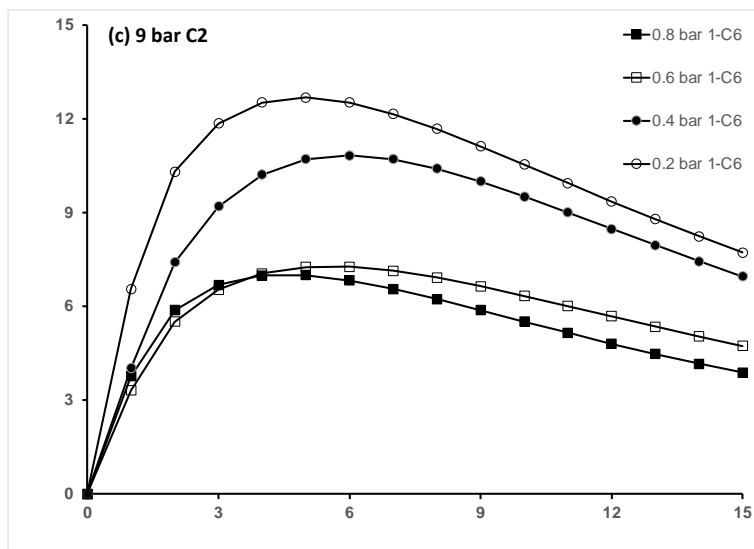
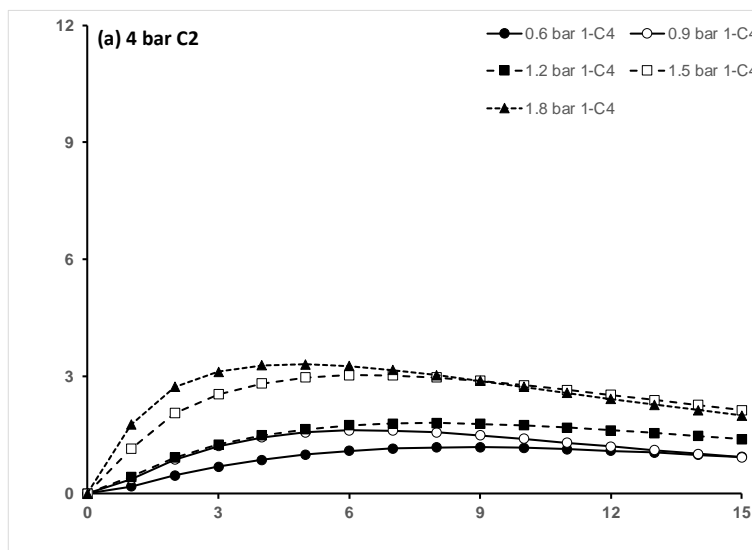


Figure S6: Gas phase ethylene/1-hexene copolymerization rate curves at different levels of 1-hexene (a) 4 bar ethylene (b) 7 bar ethylene (c) 9 bar ethylene at 70°C.



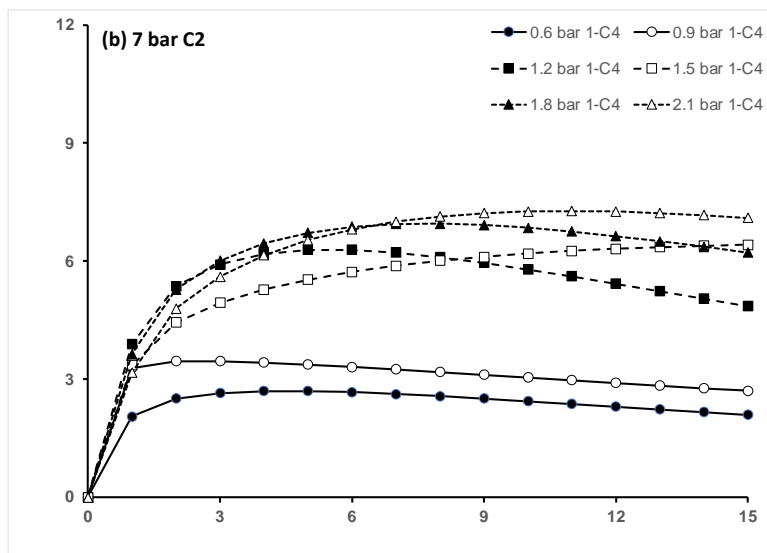
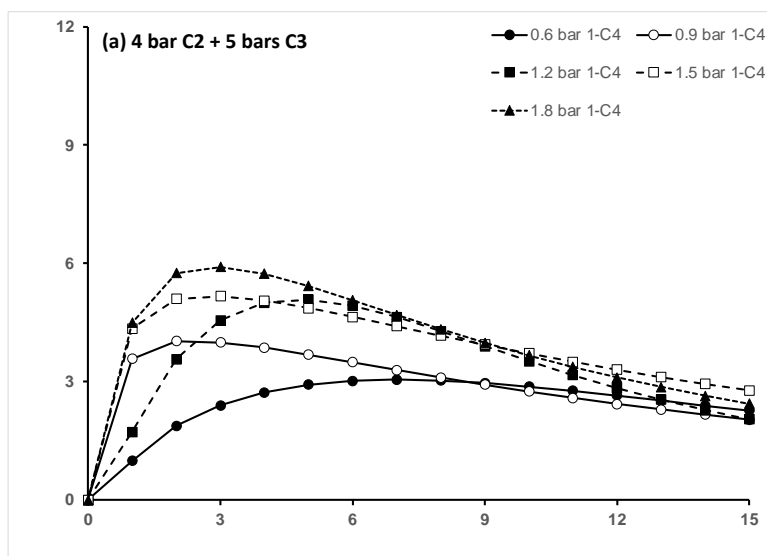


Figure S7: Gas phase ethylene/1-butene copolymerization rate curves at different levels of 1-butene and (a) 4 bars and (b) 7 bar ethylene at 70°C.

S3.2 Quaternary Systems

The rate profiles for the ethylene co-1-butene system in the presence of propane (C3), iso-butane (iC4) and normal pentane (nC5) shown in Figure S8, S9 and S10 respectively.



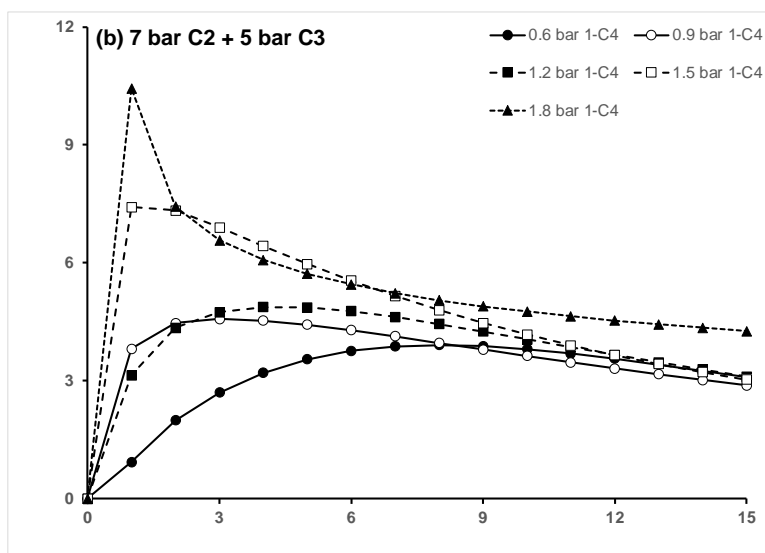


Figure S8. Rate of polymerization of (a) 4 bars and (b) 7 bars of ethylene in the presence of 5 bars of C3 and various 1-C4 concentrations at 70°C.

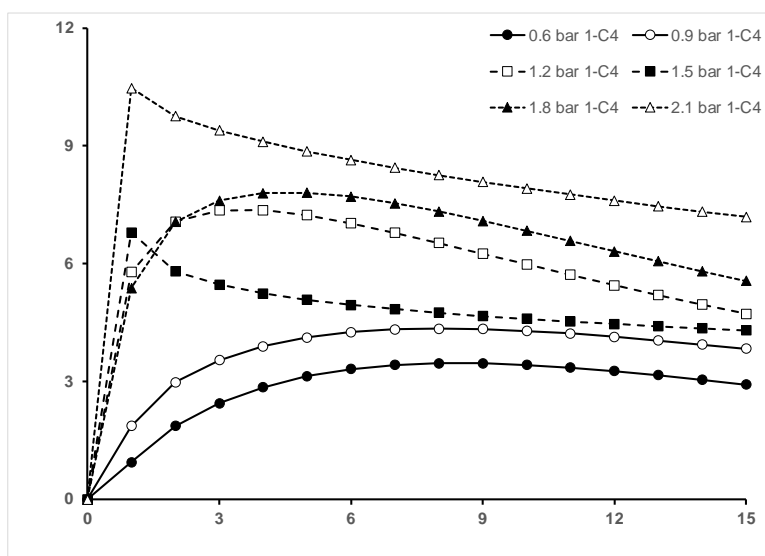


Figure S9. Rates of polymerization for 7 bars of C2 both in the presence of 3 bars of iC4 and various concentrations of 1-C4.

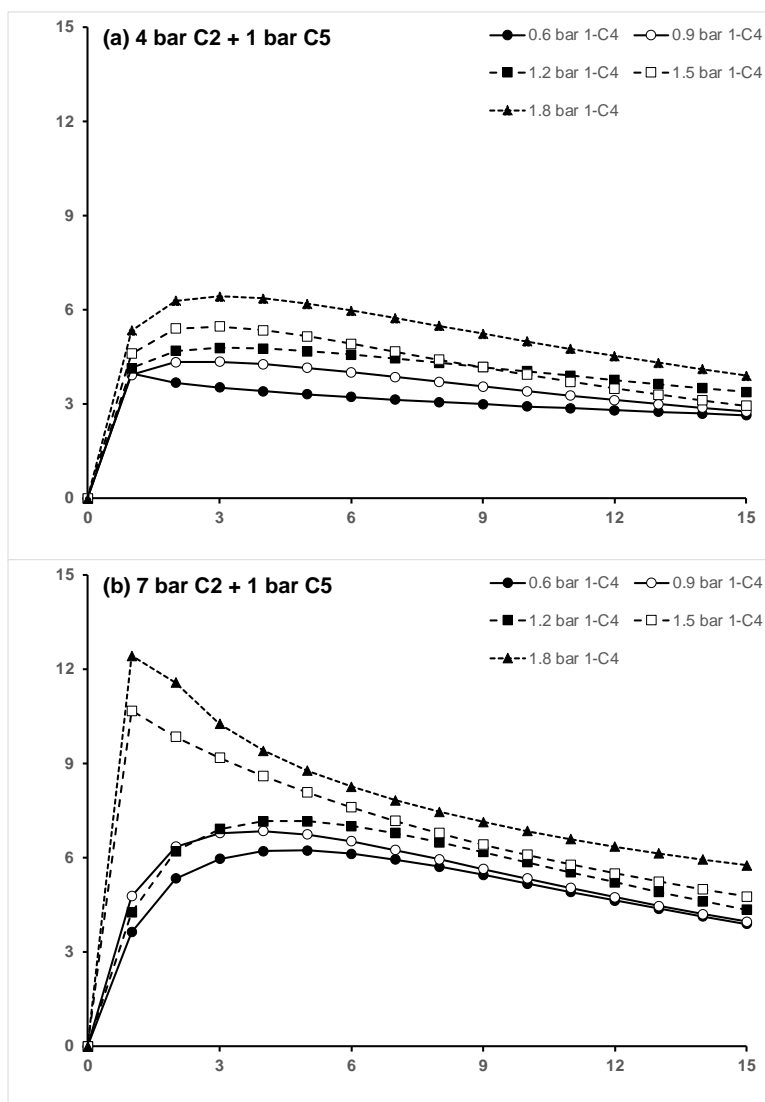


Figure S10. Rate of polymerization of (a) 4 bars and (b) 7 bars of ethylene in the presence of 5 bars of C3 and various 1-C4 concentrations at 70°C.

S4. References

- 1 Seber GAF, Wild, C. J. (1989) Nonlinear regression. New York: Wiley
- 2 Mehdiabadi S, Soares JoB (2016) Quantifying the copolymerization kinetics of ethylene and 1-octene catalyzed with rac-Et (Ind) $2ZrCl_2$ in a solution reactor. *Macromolecules* 49 (7):2448-2457
- 3 A. Ben Mrad, N. Sheibat-Othman, S. Norsic, T.F.L. McKenna, Multicomponent Solubility of Vapors in Polyethylene: an experimental and theoretical analysis, *Ind. Eng. Chem. Res.*, 60 (2020) 10791-10806
- 4 Alizadeh A, Chmelař J, Sharif F, Ebrahimi M, Kosek J, McKenna TF (2017) Modeling condensed mode operation for ethylene polymerization: part I. Thermodynamics of sorption. *Industrial & Engineering Chemistry Research* 56 (5):1168-1185
- 5 Sanchez IC, Lacombe RH (1976) An elementary molecular theory of classical fluids. Pure fluids. *The Journal of Physical Chemistry* 80 (21):2352-2362
- 6 Bashir MA, Ali MA-h, Kanellopoulos V, Seppälä J (2013) Modelling of multicomponent olefins solubility in polyolefins using Sanchez–Lacombe equation of state. *Fluid Phase Equilibria* 358:83-90