Exploratory study on the viscosity of Poly(ethyleneglycols) and their mixtures with CO_2

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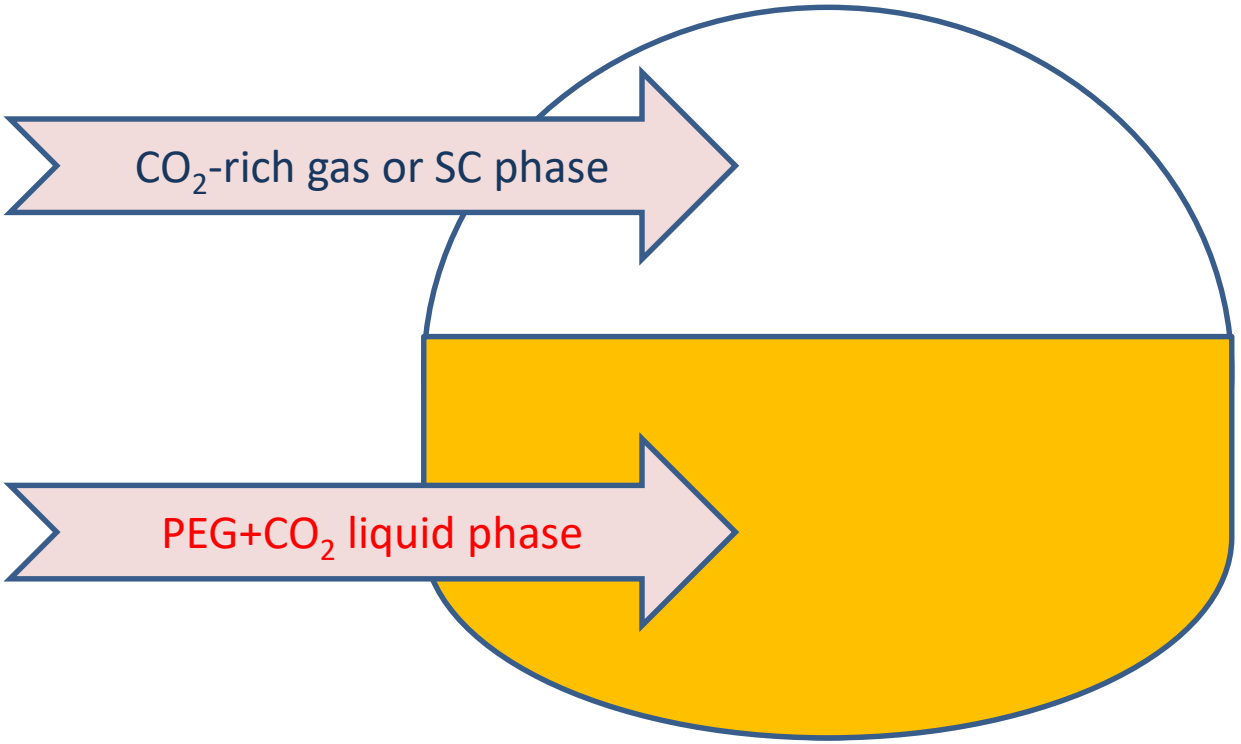
The systems we will be talking about

2 phases in equilibrium! We aim to correlate/estimate the viscosity of the LIQUID PHASE: PEG saturated with CO_2



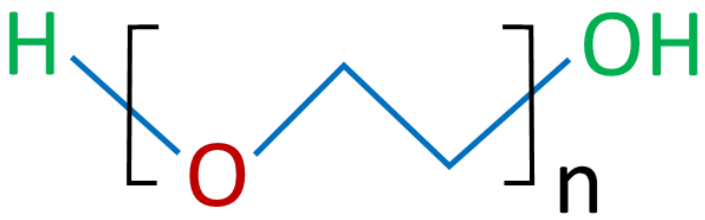
Motivation

- PEGs are “green” sustainable solvents used in a large number of industrial applications.
- PEGs are a useful model for several important fluids and applications.
- Saturation of polymers with CO_2 is often used as a **plasticizer** or **fluidizer.**
- CO_2 has been widely used for **enhanced oil recovery**. The study of the viscosity of a liquid phase consisting of PEGs saturated with CO_2 may contribute to the modelling of that industrial process.

Ultimate Goal

Development of a correlation scheme capable of predicting the viscosity of PEGs saturated with CO_2, from their molar mass and the smallest possible number of empirical parameters.

Possibly not an easy task! Keesom intermolecular forces are potentially important!



Permanent multipoles
Intra and intermolecular “hydrogen bonds”

Strong quadrupole moment

Sequence of the presentation

1. We will show the general type of correlation, for the viscosity of the mixture, we are exploring to reach this goal.
2. We will show that the prospects are good, as long as the viscosity for the single components are known.
3. We will show that it is possible to estimate the viscosity of PEGs at high pressure with reasonable accuracy, using their molar mass and their viscosity under 0.1 MPa, only (tests with PEG200 and PEG400).

Viscosity of (PEG+CO_2) mixtures

Correlation by the

method of Grunberg and Nissan for a binary mixture

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}$$

1 – PEG

2 – CO_2

x_1, x_2 – mass fractions (for the present work)

G_{12} is an interaction parameter .

Procedure

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}$$

- η_1 from experimental viscosity data at high pressures for PEG 400 [1] and for PEG 200 [2] **or by an ESTIMATION technique (see ahead).**

- η_2 from NIST REFPROP v.7.

- x_1 ***and*** x_2 from Sanchez-Lacombe EOS [3]

- G_{12} interaction parameter dependent on the species and on T and p.

Note: The dependence on p is related to CO_2 solubility – ***and dependence on composition may happen*** – see extensive study published by ***J. Isdale***… *(Symp. Transp. Prop. Fluids and Fluid Mixtures, NEL, 1979)*

[1] M.C.M. Sequeira, M.F.V. Pereira, H.M.N.T. Avelino, F.J.P. Caetano, J.M.N.A. Fareleira, **Fluid Phase Equilib. 496 (2019) 7–16**. https://doi.org/10.1016/j.fluid.2019.05.012

[2] M.C.M. Sequeira, H.M.N.T. Avelino, F.J.P. Caetano, J.M.N.A. Fareleira, to be published.

[3] D. Gourgouillon, M. Nunes da Ponte, Phys. Chem. Chem. Phys. 1 (1999) 5369-5375.

Requirements:

1. A correlation/prediction method must be developed for the viscosity of mixtures of PEGs saturated with CO_2 as a function of the temperature and the CO_2 solubility (or pressure).

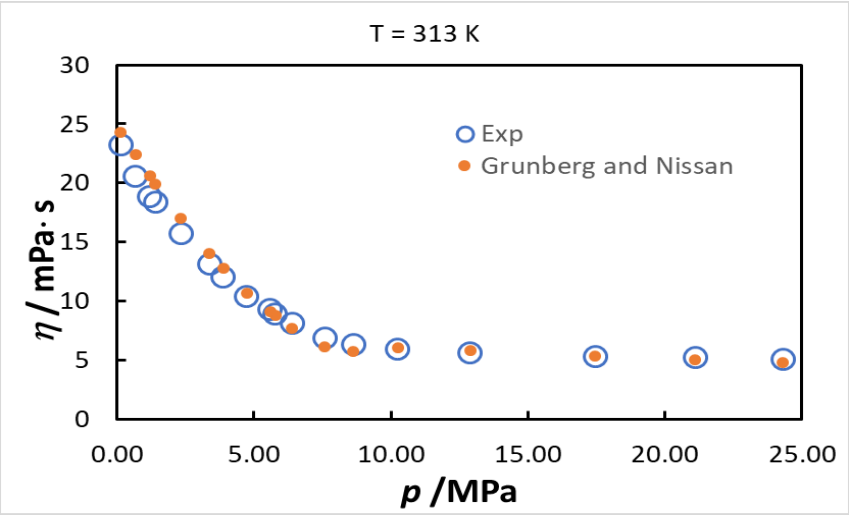
2. The correlation scheme must be based on experimental viscosity and density results at high pressures for a homologous series of glycols – Di, Tri, and Tetra ethylene glycols (DiEG, TriEG,TeEG).

3. A single correlation method must be developed to describe the viscosity of the above substances, and to predict the viscosity of PEGs as a function of pressure just from atmospheric pressure data. Tests will be carried out for PEG 200 and PEG 400.

In the following slides, we show the results based on the determination of the interaction parameter G_{12} for systems (PEG+CO_2) using the experimental data for the viscosity of **CO_2 saturated mixtures** of **PEG 200** [Avelino et al., J. Supercrit. Fluids **128** (2017) 300-307] and **PEG 400** [Gourgouillon et al. J. Supercrit. Fluids **13** (1998) 177-185] at pressures up to 25 MPa in the temperature range (313–348) K.

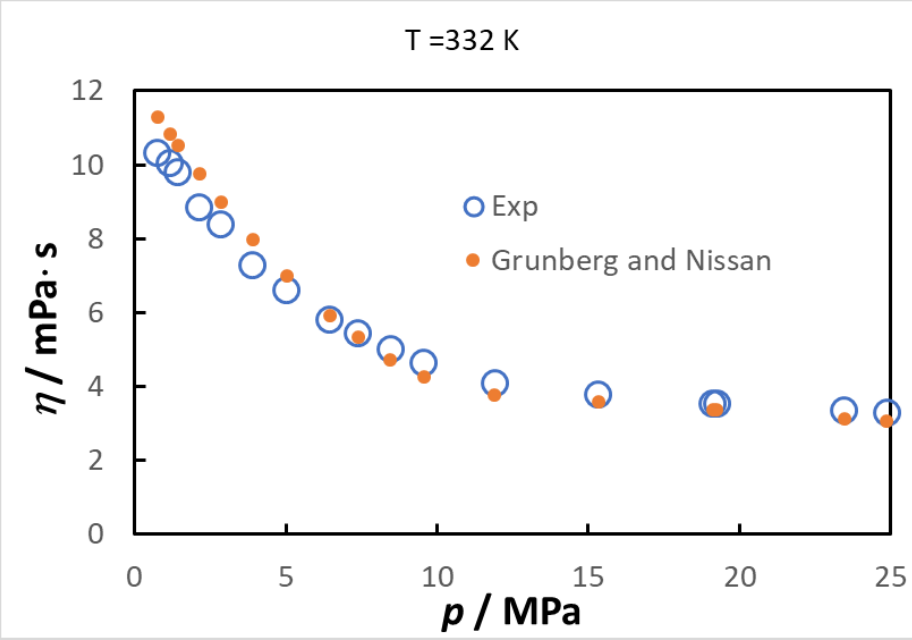
This work uses the **solubility of CO_2** in those olygomers and the **Sanchez-Lacombe EOS** as published by **Gourgouillon and Nunes da Ponte [Phys. Chem. Chem. Phys. 1 (1999) 5369-5375]**.

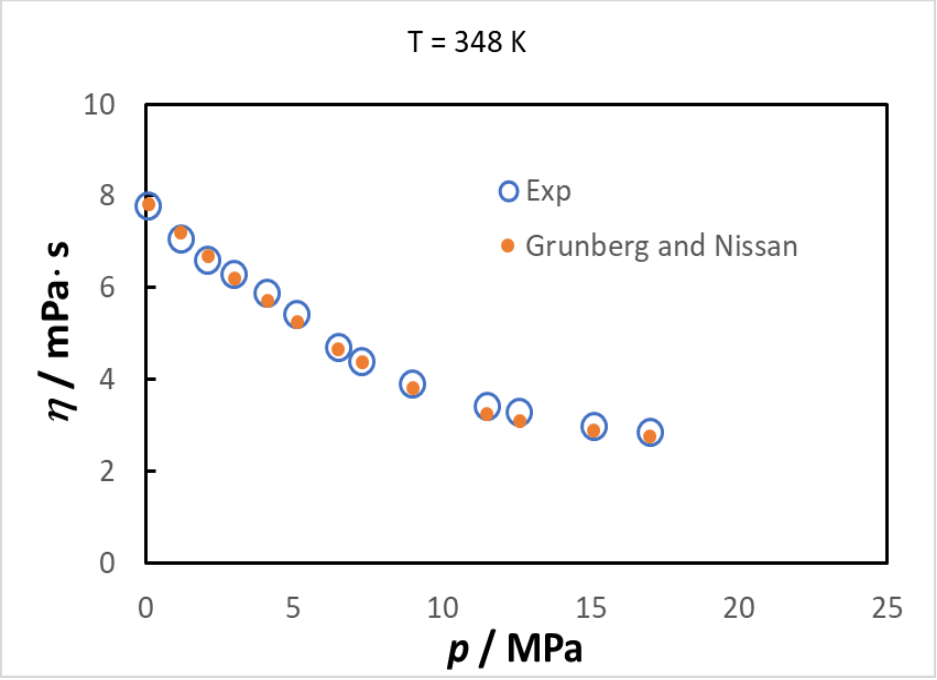
Comparison of Grunberg and Nissan equation (by fitting G_{12}) with experimental viscosity values for the system (PEG 200 + CO_2)[4]



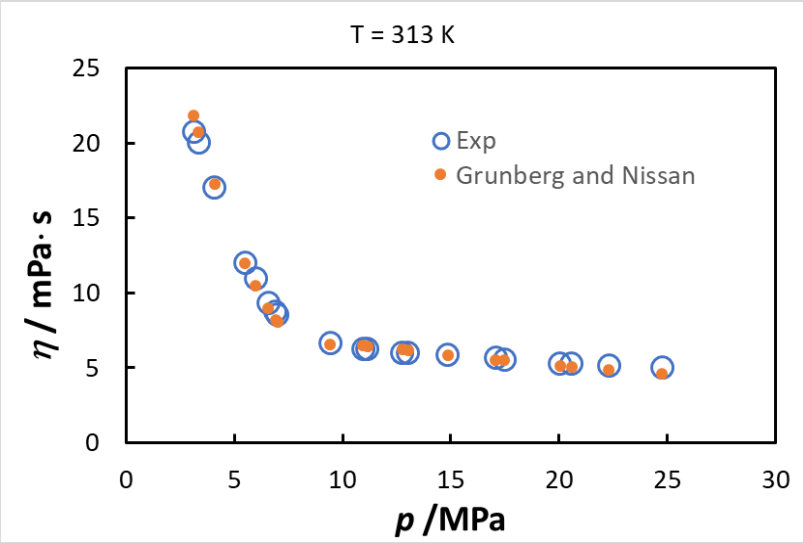
[4] Avelino et al., J. Supercrit. Fluids 128 (2017) 300-307.

Also using experimental viscosity data (η_1) for PEG 200 [Sequeira et al., to be published]



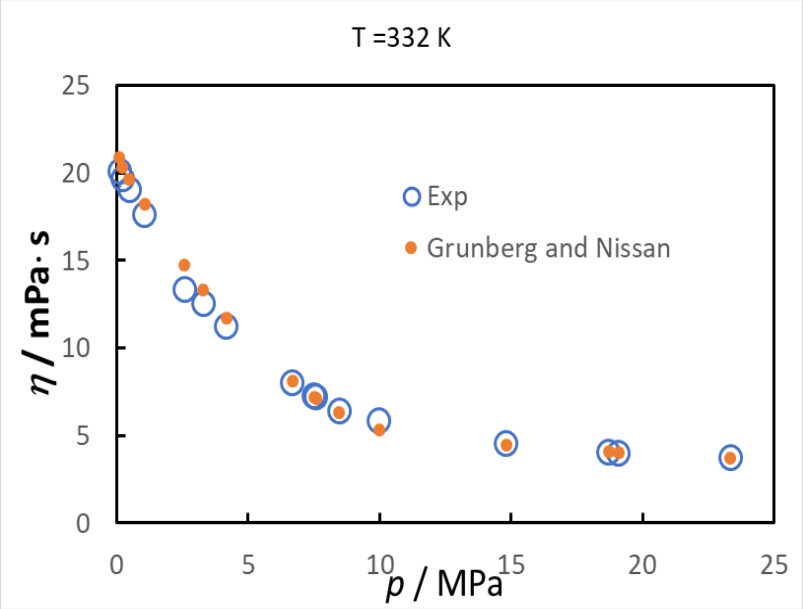


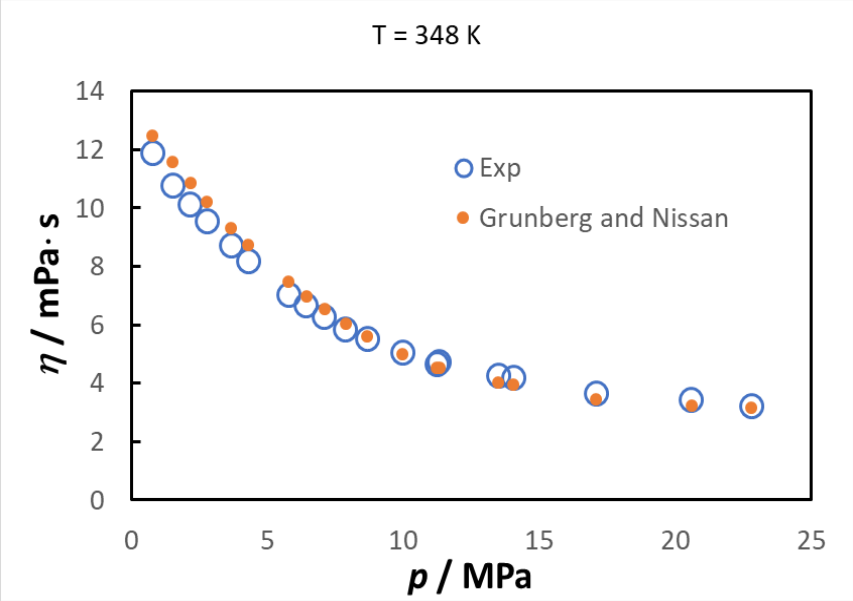
Comparison of Grunberg and Nissan equation (by fitting G_{12}) with experimental viscosity values for the system (PEG 400 + CO_2)[5]



[5] Gourgouillon et al., J. Supercrit. *Fluids* 13 (1998) 177-185.

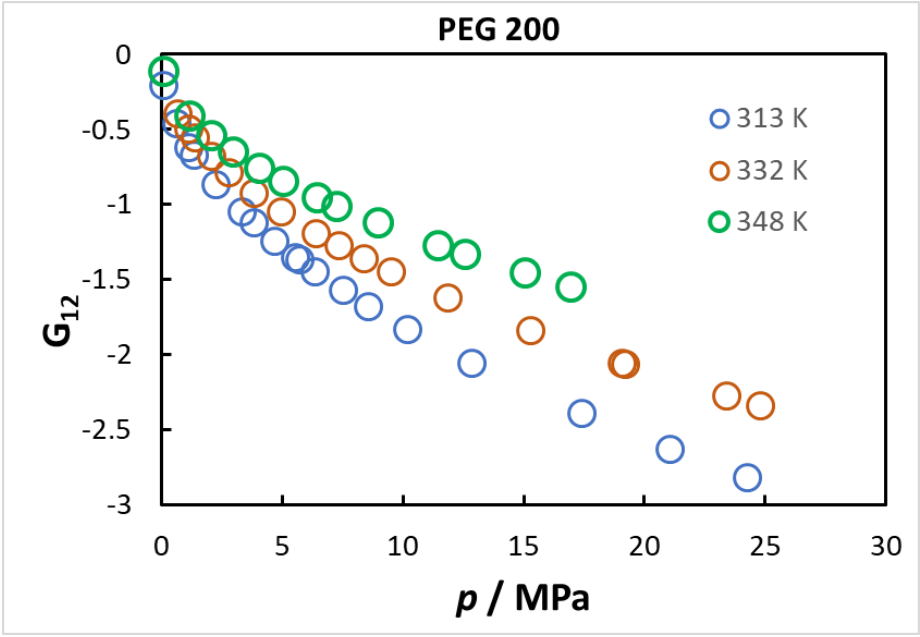
Also using **experimental** viscosity data (η_1) for PEG 400 [Sequeira et al., Fluid Phase Equilib. 496 (2019) 7–16

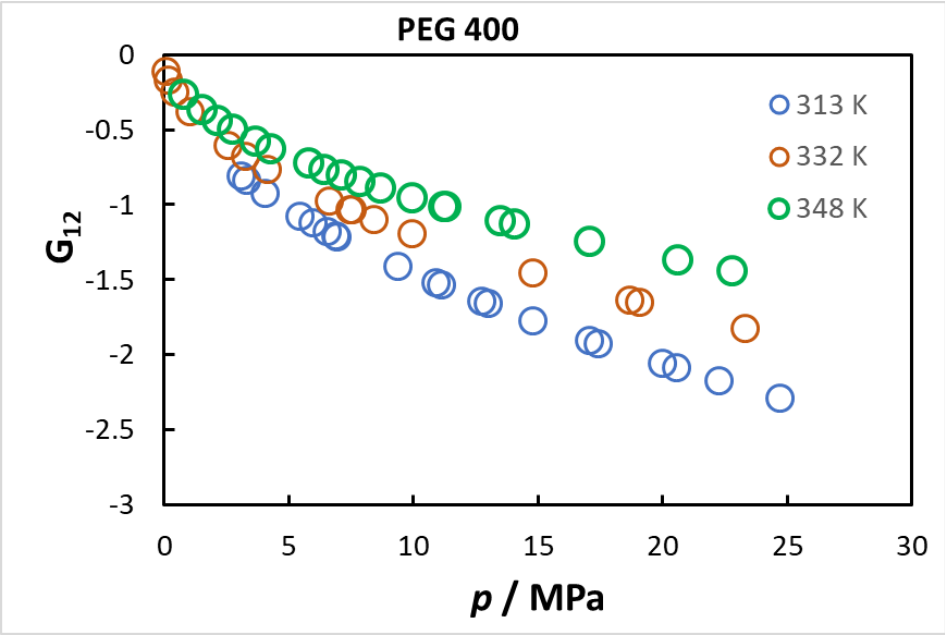




G_{12} obtained by fitting for both PEGs + CO_2

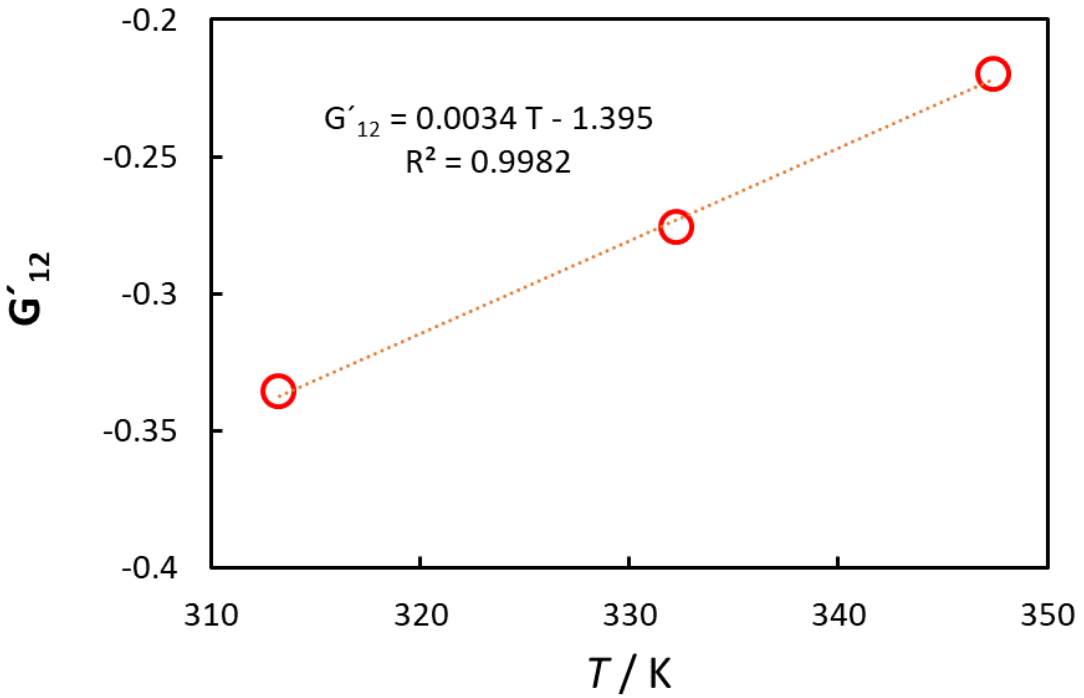
Variation with temperature and pressure





$$G_{12} = G'_{12}\, M^{n}\, p^{0.5}$$

G_{12} can be decomposed as a product of functions of the molar mass and CO_2 pressure (or composition). Then G'_{12}, should depend on the temperature only.



G'_{12} has the same value for PEG 200 and PEG 400

Note: G'_{12} and n calculated by fitting: n= -0.340 for both PEGs

Often, experimental viscosity data for PEGs at pressures higher than 0.1 MPa will not be available.

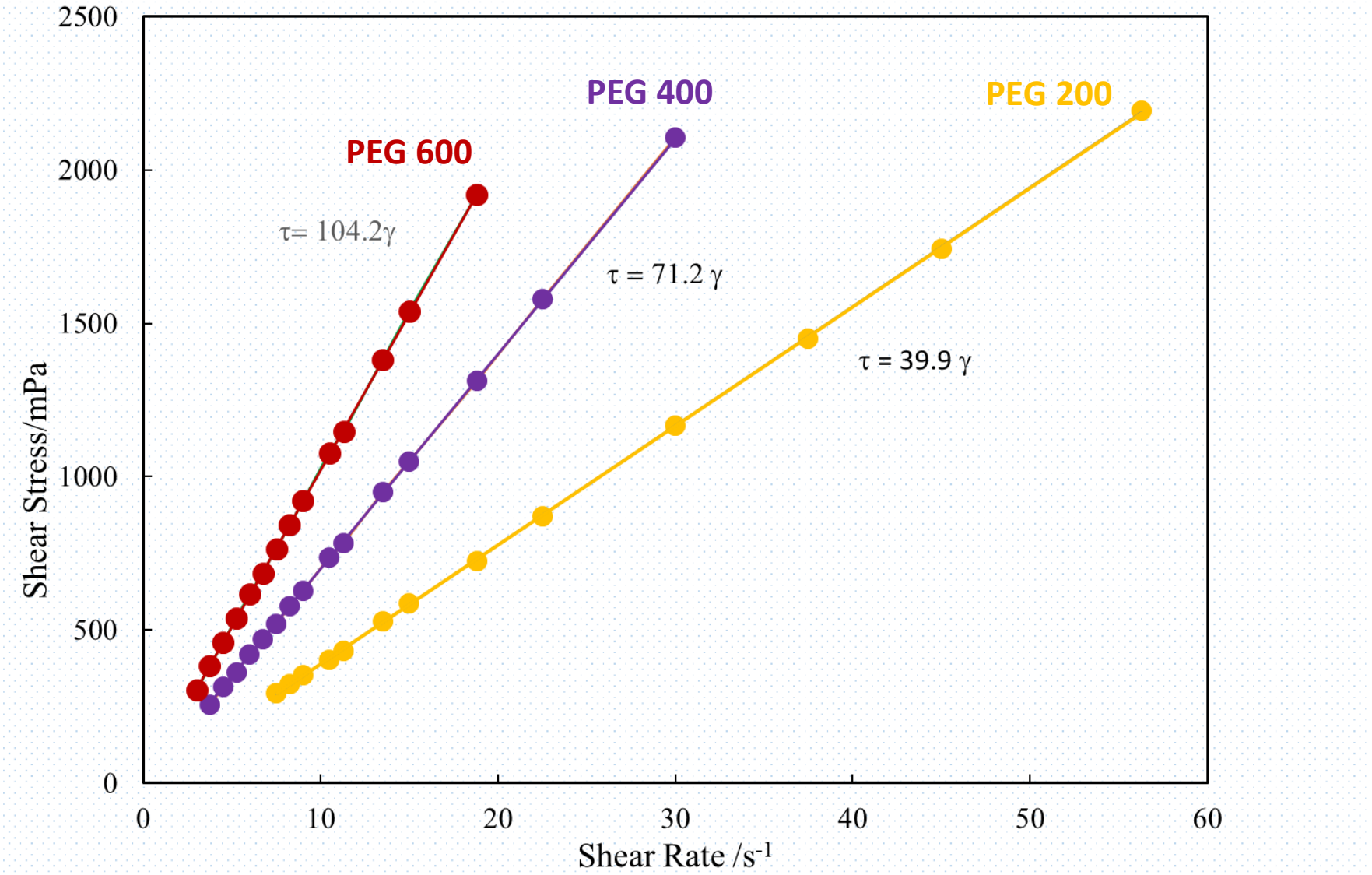
Therefore, a scheme to estimate the viscosity of PEGs at high pressures has been developed.

Tests were carried out for PEG 200 and PEG 400 for pressures up to 50 MPa in the temperature range (293–348) K.

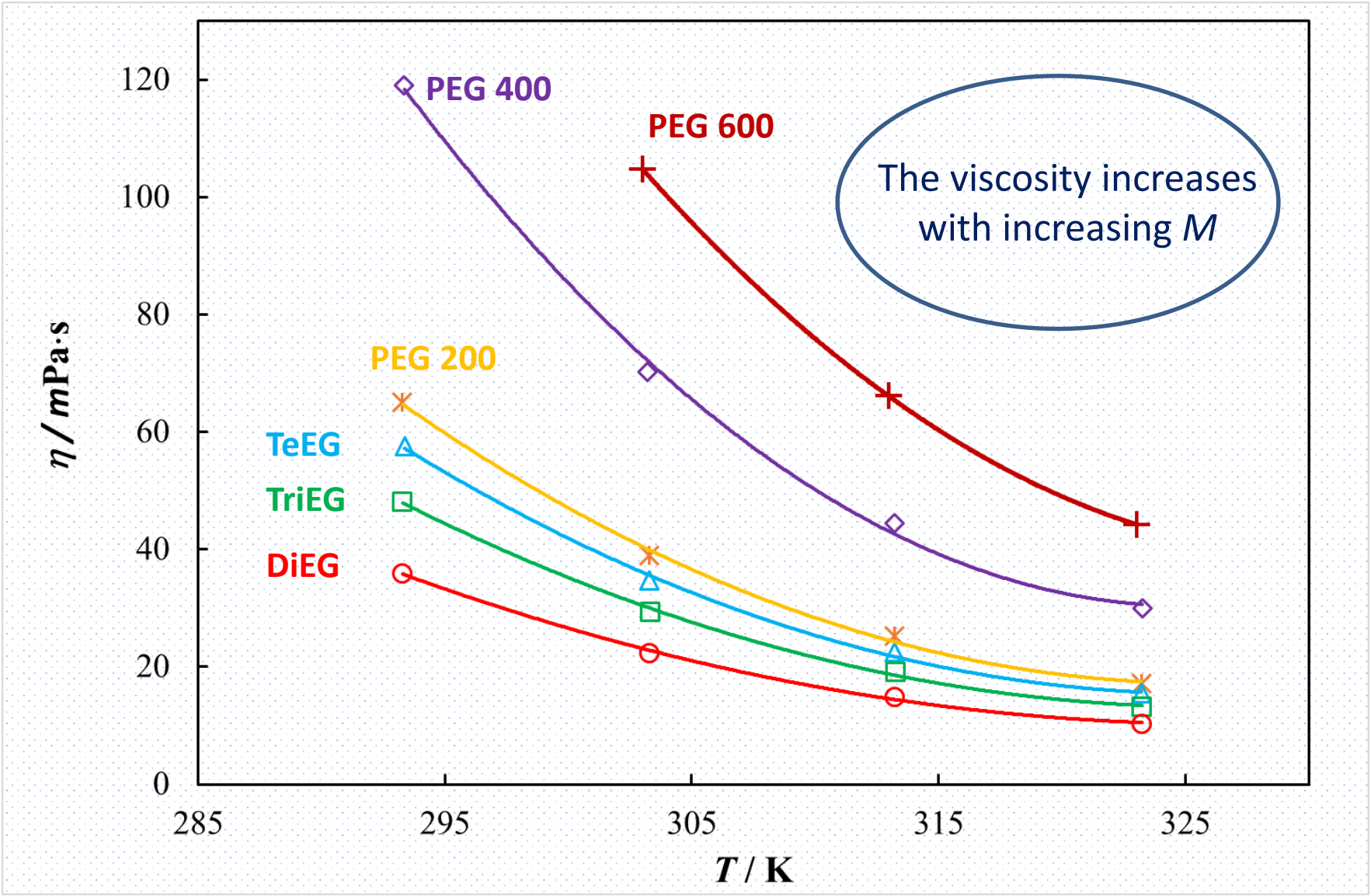
The necessary density data for ethylene glycols and the PEGs have been measured by our group.

A characterization of the fluids involved in the present study will follow…

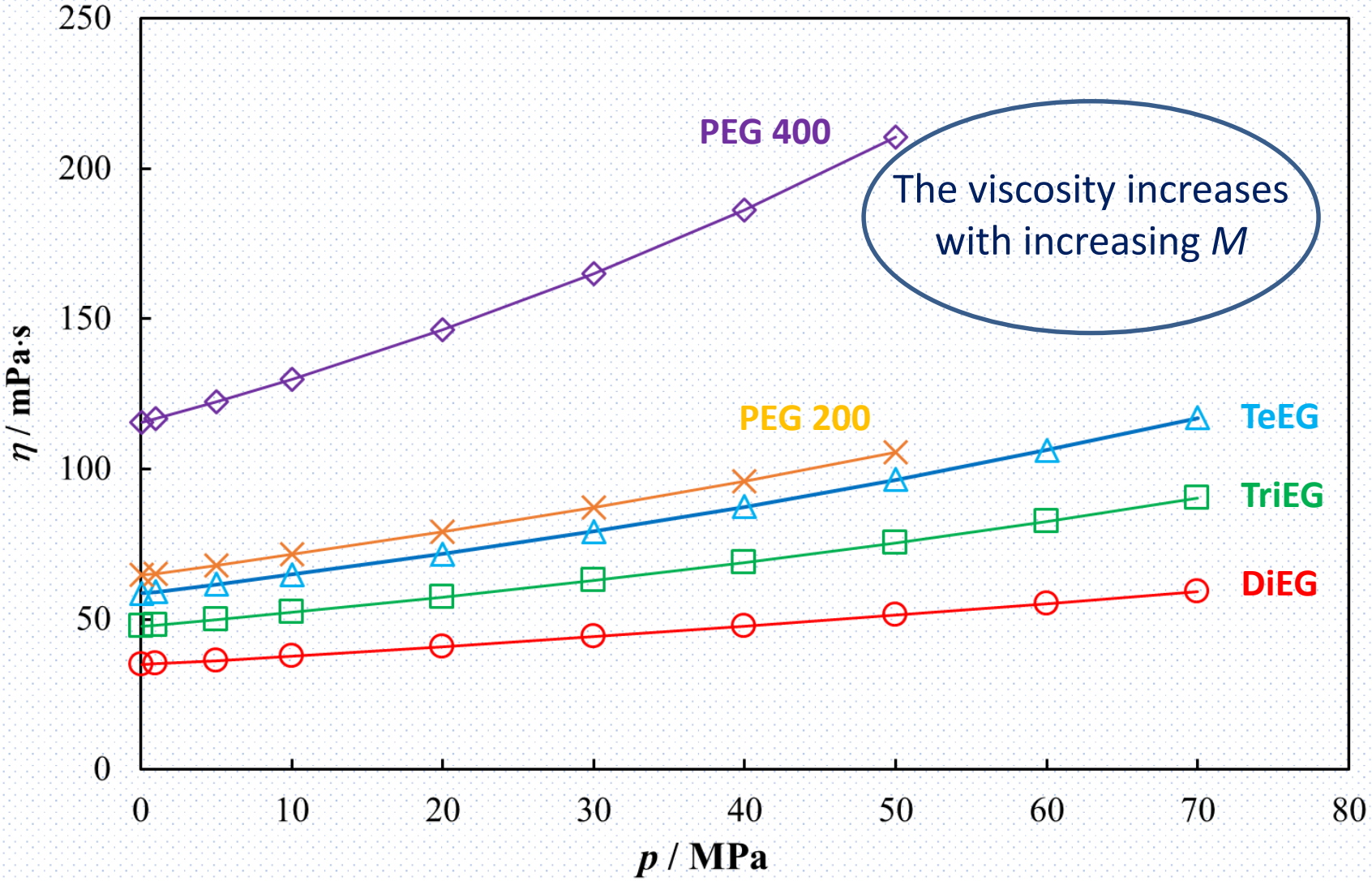
Newtonian Behaviour of PEGs at 303 K



Effect of molar mass, *M*, on the viscosity at 0.1 MPa



Influence of molar mass on the viscosity as a function of pressure at 293 K



Backbone of the Correlation/Estimation method: Correlation of viscosity of Ethylene Glycols with the molar volume

Heuristic development [1] of the kinetic theory of a dense hard-sphere fluid applied to the van der Waals model of a fluid [2]

$$\eta^* = 6.035\times10^8 V_m^{2/3} \times \left(MRT\right)^{-1/2} \times \eta / R_\eta$$

R_η *is a r*oughness factor, dependent on the chain length

$$\frac{1}{\eta^*} = \sum_{i=0}^{5} a_i \left(\frac{V_m}{V_0}\right)^i$$

Dependent on V_m, only!

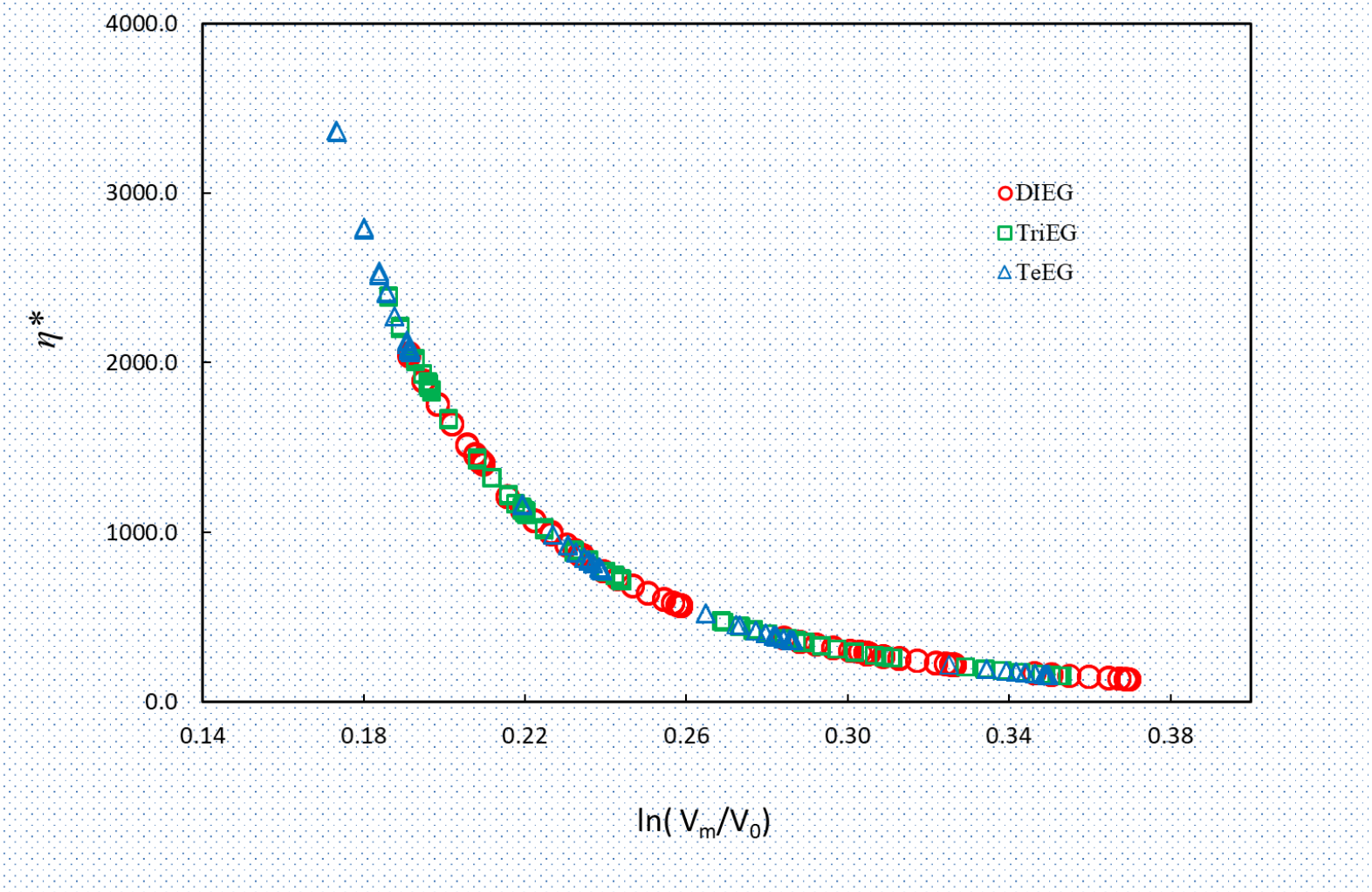
$$V_0\left(T\right) = V_{0,ref} + l\left(T - T_{ref}\right) + m\left(T - T_{ref}\right)^2$$

Dependent on T only!

[1] S.F.Y. Li, R.D. Trengove, W.A. Wakeham, M. Zalaf, The transport coefficients of polyatomic liquids, Int. J. Thermophys. 7 (1986) 273–284. doi:10.1007/BF00500154.

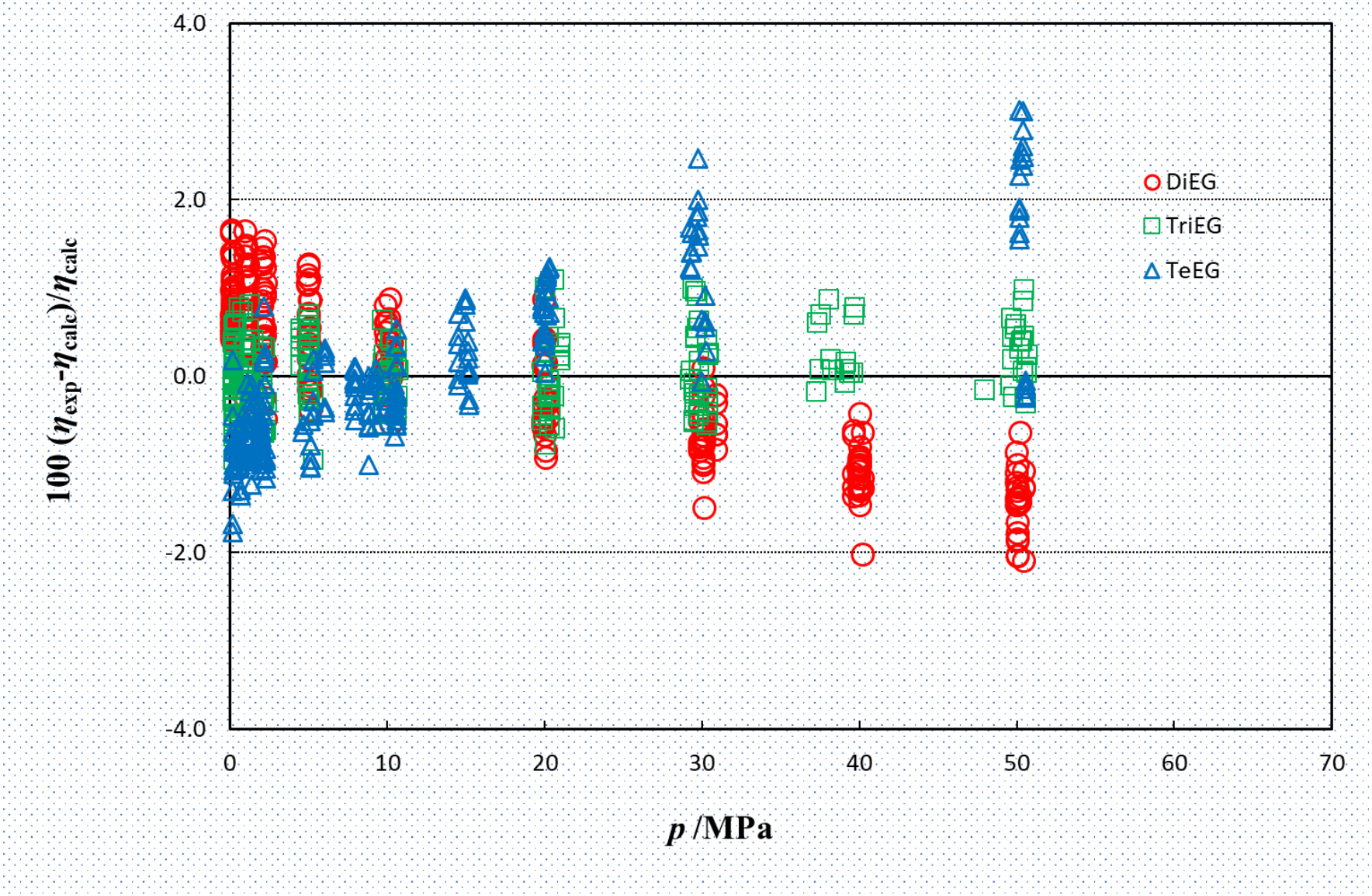
[2] J.H. Dymond, Corrected Enskog theory and the transport coefficients of liquids, J. Chem. Phys. 60 (1974) 969–973. doi:10.1063/1.1681175.

Hard-Spheres Correlation for ethylene glycols (DiEG,TriEG,TeEG)

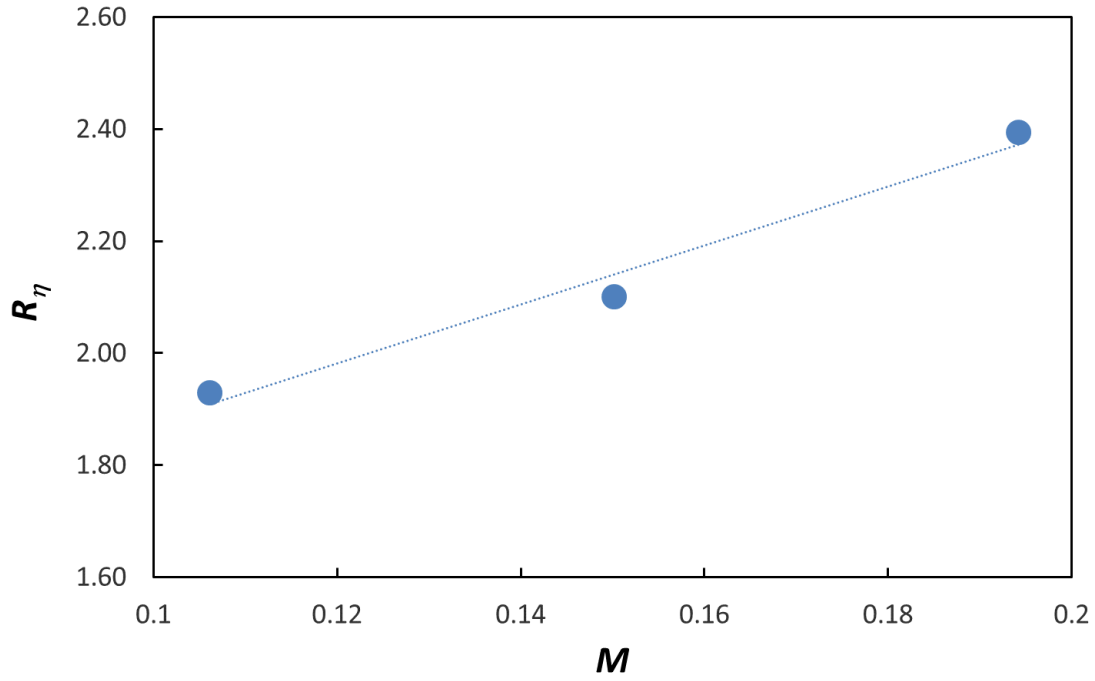


One single equation, allowing interpolation of the viscosity of three ethylene glycols in the pressure and temperature with uncertainty about 1.5 %, at a 2σ level.

Deviation of viscosity data from the Hard-Spheres correlation as a function of pressure



Roughness Coefficients, *R*η, for DiEG, TriEG, and TeEG as a function of the molar mass, *M*



$$R_\eta = 1.3498 + 5.2675 \times M$$

This linear correlation was used to estimate

***R*η for PEG 200 and PEG 400**

How to **estimate** the viscosity of PEGs as a function of pressure

1st: The following equation will be used as a **reference** for the estimation technique

These parameters are the same as for the series of ethylene glycols

$$\frac{1}{\eta^*} = \sum_{i=0}^{5} a_i \left(\frac{V_m}{V_0} \right)^i$$

2nd: Calculation of $V_0(T)$ from a datum for viscosity at 0.1 MPa, calculating…

$$\eta^*(0.1\text{MPa}) = 6.035\times10^8 V_m(0.1\text{MPa})^{2/3} \times \left(MRT\right)^{-1/2} \times \eta(0.1\ \text{MPa}) / R_\eta$$

with $R_\eta(\text{PEG}) = 1.3498 + 5.2675 \times M$

$$\frac{1}{\eta^*(0.1\ \text{MPa})} = \sum_{i=0}^{5} a_i \left(\frac{V_m(0.1\ \text{MPa})}{V_0} \right)^i$$

Calculating V_0 from **atmospheric pressure** viscosity datum for each PEG at a given temperature

How to estimate the viscosity of PEGs as a function of pressure

3rd: Estimation of the viscosity of PEGs in a range of temperatures and pressures

Using the reference equation again η* is obtained:

$$\frac{1}{\eta^*(T,p)} = \sum_{i=0}^{5} a_i \left(\frac{V_m(T,p)}{V_0} \right)^i$$

Calculated from **atmospheric pressure** viscosity datum for each PEG at a given temperature

And, finally, the viscosity:

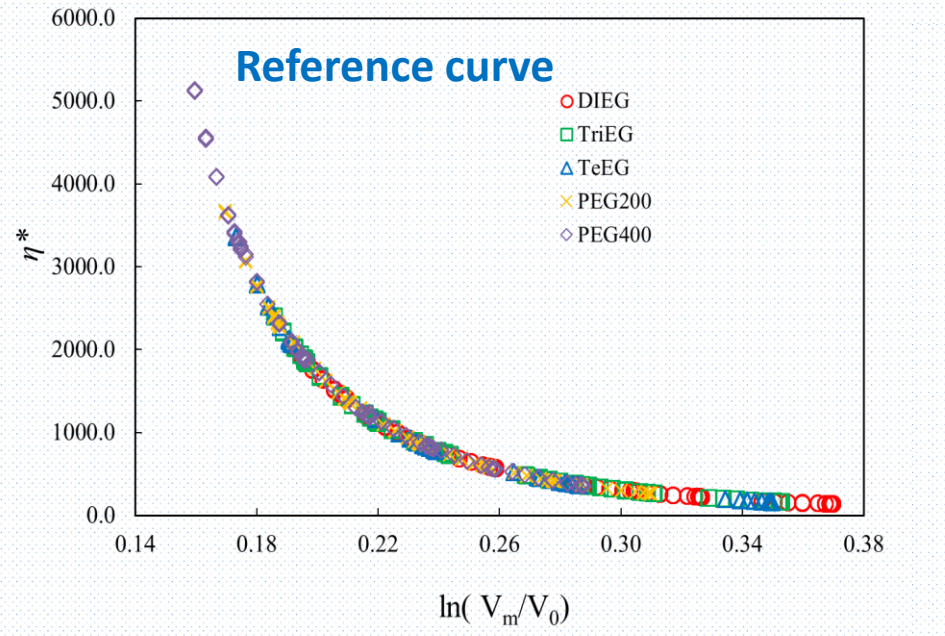
$$\eta(T,p) = \left(6.035 \times 10^8\right)^{-1} \times [V_m(T,p)]^{-2/3} \times (MRT)^{1/2}\, \eta^*(T,p) \times R_\eta$$

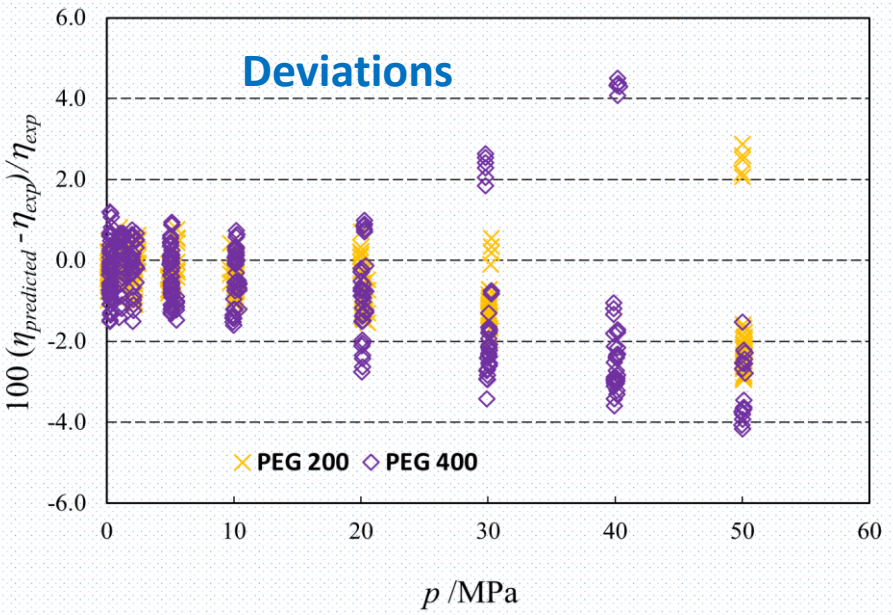
with $R_\eta(PEG) = 1.3498 + 5.2675 \times M$

Estimating the viscosity of PEGs at high pressures

The correlation equation built for ethylene glycols was used as a reference to estimate the viscosity of PEG 200 and PEG 400 at high pressures, using one datum at 0.1 MPa at each temperature. Deviations of the experimental viscosity data from the estimated values are ca. 2.0 % (PEG 200) and 3.4 % (PEG 400), at 2 σ level.

Systematic increase with pressure is NOT a problem regarding our final aim to predict the effect of CO_2 addition on the viscosity of (PEGs+CO_2): for $p >> p_c$, is EASY to predict!





Conclusions and work in progress

The results of this exploratory work were quite satisfactory. However, some extra work must be carried out, in order to complement the study.

Namely,

- Tests of the present predictive scheme, involving the estimation of the viscosity of other PEGs (with higher molar mass) at high pressure, and the estimation of the parameter G_{12} for their saturated mixtures with CO_2.
- Simultaneous correlation of viscosity and self-diffusion of ethylene glycols, using a hard-spheres method. (As it was done for alkyl adipates)
- Study by NMR spectrometry of the dynamics of the chains of di, tri and tetra ethylene glycols by measuring the spin lattice relaxation times T_1 of ^{13}C and protons.

Thanks for your attention!

But, this is not all!…
This is…

To be continued

Thanks to Project UID/QUI/00100/2013 and Project UID/QUI/00100/2019 funded by **Fundação para a Ciência e a Tecnologia (FCT), Portugal.**

CO_2

- T_c=304.19 K
- p_c= 7.38 MPa

1st – Basis of the Predictive Scheme : EXPERIMENTAL DATA for Glycols and PEGs

a) Experimental viscosity (and density) data for di-, tri, and tetra-ethylene glycols at high pressures to **build a viscosity correlation/prediction scheme** using the molar mass as a parameter. From Marta F Pereira; Helena Avelino; Fernando Caetano; João Fareleira, Fluid Phase Equilibria

b) Experimental viscosity (and density) data at high pressures for PEG 400 (in Fluid Phase Equilibria ….) and for PEG 200 (submitted to publication …..) to extend **the scheme** to predict the viscosity of PEGs from the scheme based on the data in a).

Method of Grunberg and Nissan for a binary mixture

$$\ln \eta_{mix} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12}$$

η_1 from our correlation for viscosity of glycols and PEGs

η_2 from experimental data (in the present case, from NIST REFPROP v. 7) for the same temperature and pressure.

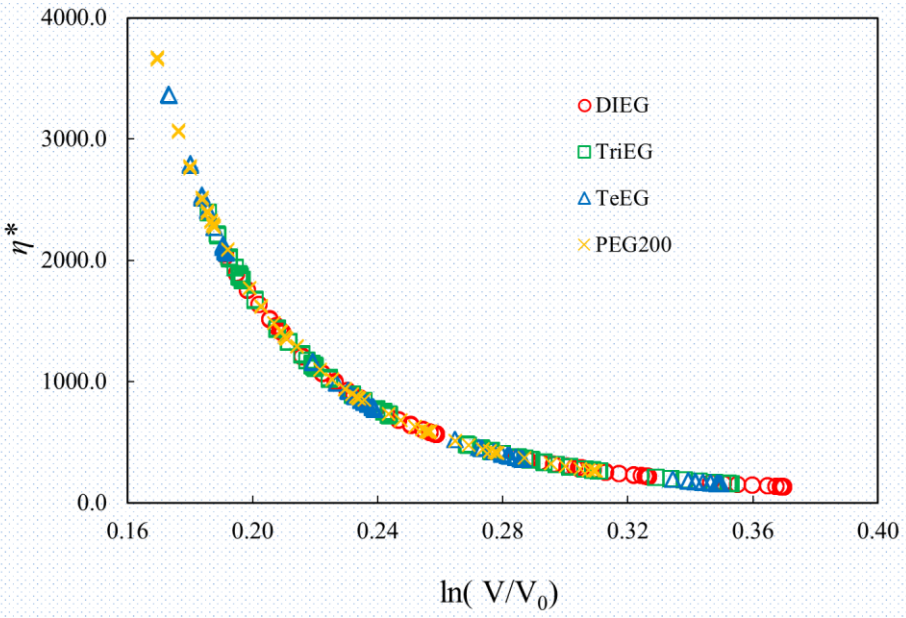
G_{12} treated as an interaction parameter dependent on 1, 2, T and p.

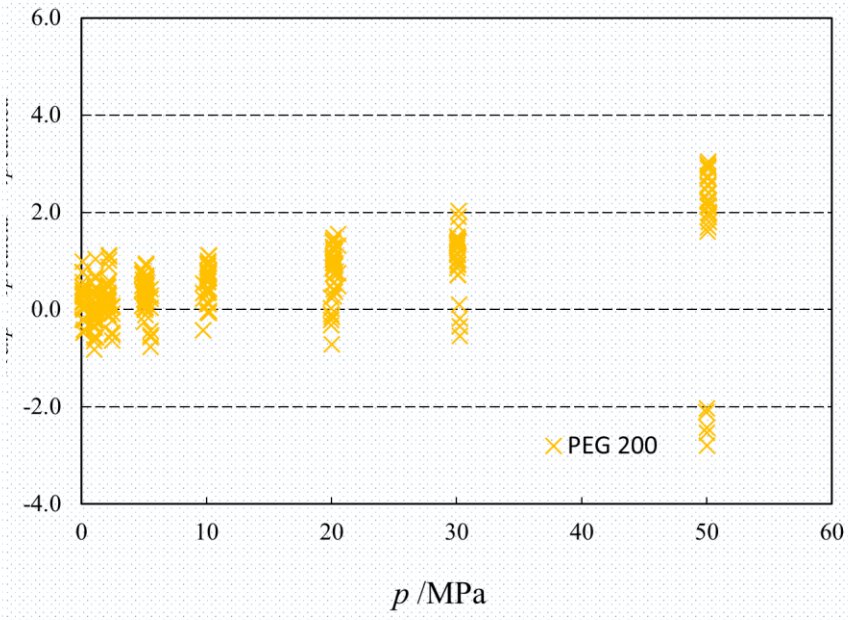
Note : In the present case, the dependence on pressure, p, is equivalent to a dependence on CO_2 solubility (i.e., the composition)

- see extensive study published by *J. Isdale*... (Symp. Transp. Prop. Fluids and Fluid Mixtures, NEL, 1979)

For PEG 200

The same curve of series of ethylene , allowing predicted the viscosity of PEG 200 in the pressure and temperature with uncertainty about 2.0 %, at a 2σ level.





Deviations of the experimental viscosity from the estimated values!