

Molecule Transferability Problem

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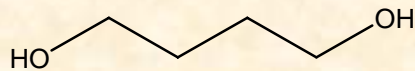
Peter Gordon (ExxonMobil)

Thomas Allison, Anne Chaka, Daniel Friend, Russ Johnson, Ray Mountain, Vince Shen (NIST)

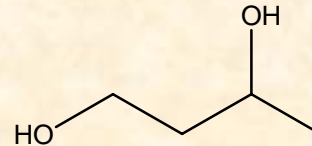
Problem Statement

- For the following molecules:

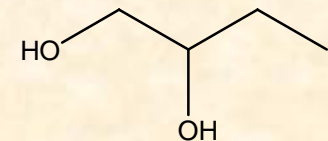
– 1,4-butanediol



1,3-butanediol



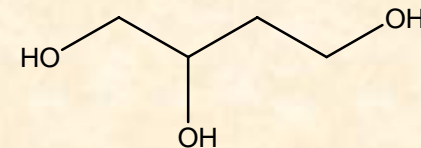
1,2-butanediol



– 2-methyl-1,3-propanediol



1,2,4-butanetriol

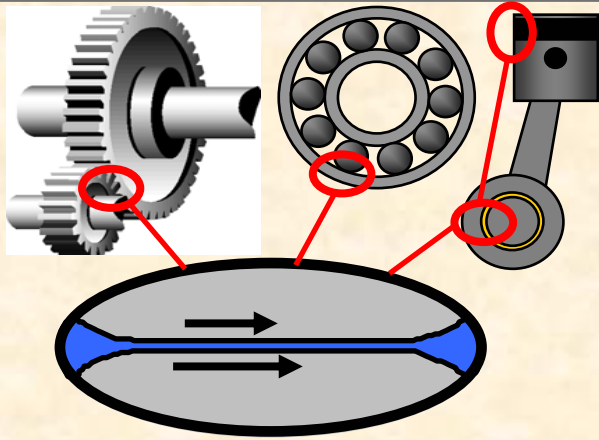


- Compute the low-strain rate limit (Newtonian) viscosity at
 - $T = 373\text{K}$, $P = 0.1\text{ MPa}$
 - $T = 373\text{K}$, $P = 250\text{ MPa}$

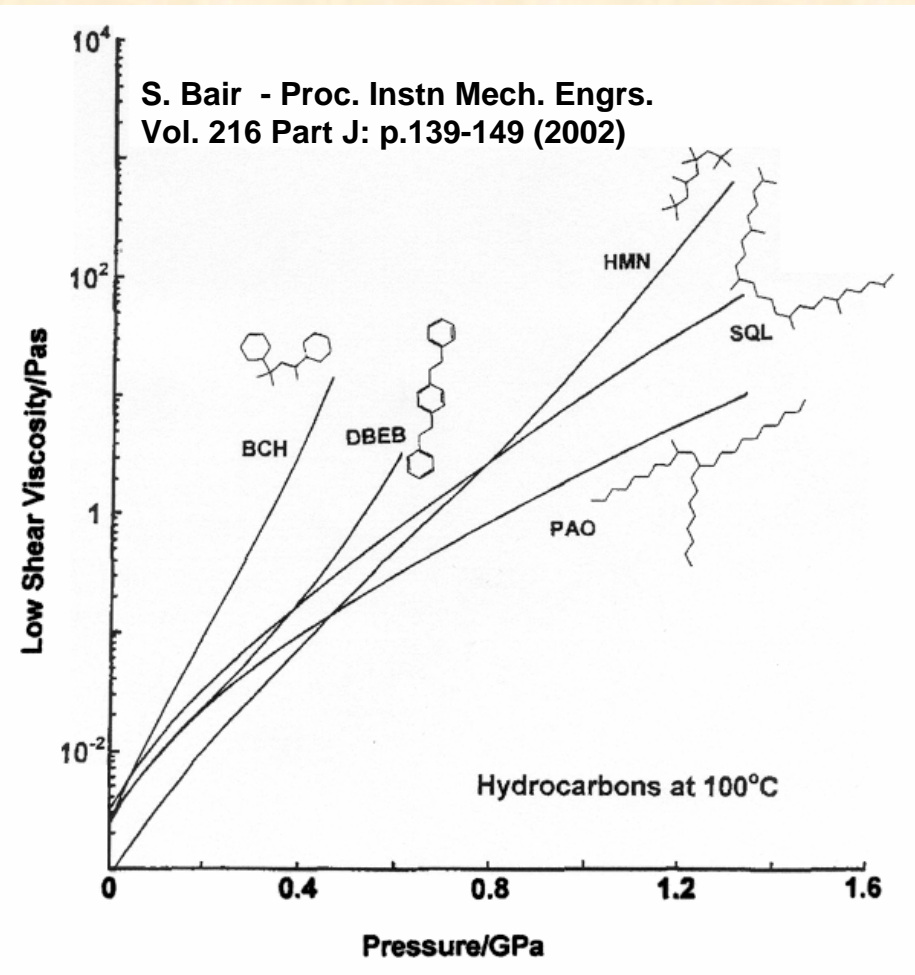
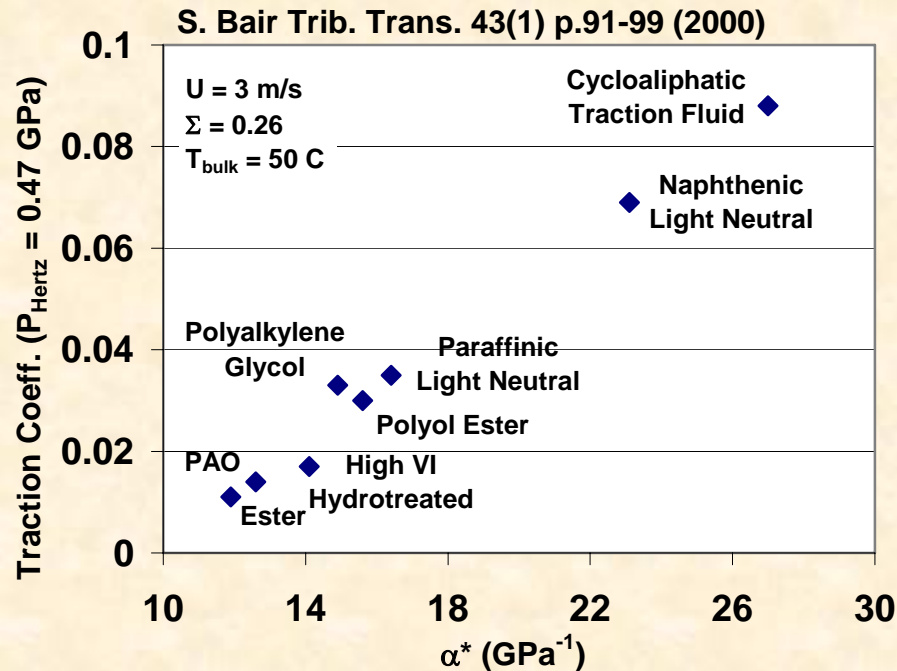
Problem Motivation

- **Viscosity is sensitive and non-linear function of molecular structure**
- **Group of related molecules collapsable into a few lumped groups (CH_x, OH)**
- **Limited available experimental data in the literature**
 - Atmospheric pressure data available for 1,n-butanediols
 - No known published data for 1,2,4-butanetriol, 2-methyl-1,3-propanediol
 - No known published data at elevated pressures for any of contest species
- **Group contribution methods not expected to perform well**
 - Isomers especially difficult in absence of second order corrections to such methods
 - Example: Sun et al (1992) – reported 100% errors at 298K and 50% at 373K using Orrick and Erbar group contribution technique for viscosity of 1,n-butanediols

Elastohydrodynamic Lubrication, Rheology & Structure-Viscosity Relationships



Average Film Thickness: $h_o \propto (U\eta\alpha)^{0.74}$



Contest Rules

- **Force field employed must be capable of describing interactions of all molecules in a consistent manner**
- **Any force field previously published in the open literature prior to contest announcement may be used**
- **New Force fields may be parameterized using any physical property data (including viscosity) with the exception:**
 - **No data from diol, triol, or n-ol species may be used**
- **State points are specified at constant pressure**
 - **If constant density ensembles are used to compute viscosity, the density chosen must be shown to be consistent with the pressure of the target state point**

Entries

“Prediction of viscosities and vapor-liquid equilibria for five polyhydric alcohols by molecular simulation”

J. L. Rafferty, M. S. Kelkar, J. I. Siepmann and E. J. Maginn
University of Minnesota, University of Notre Dame

“Viscosity of alkanol molecules using simulations with a polarizable force field”

D. van der Spoel and P. J. van Maaren
Uppsala University

“Prediction of shear viscosities using periodic perturbation method and OPLS force field”

L. Zhao, X. Wang, L. Wang, Huai Sun
Shanghai Jiao Tong University

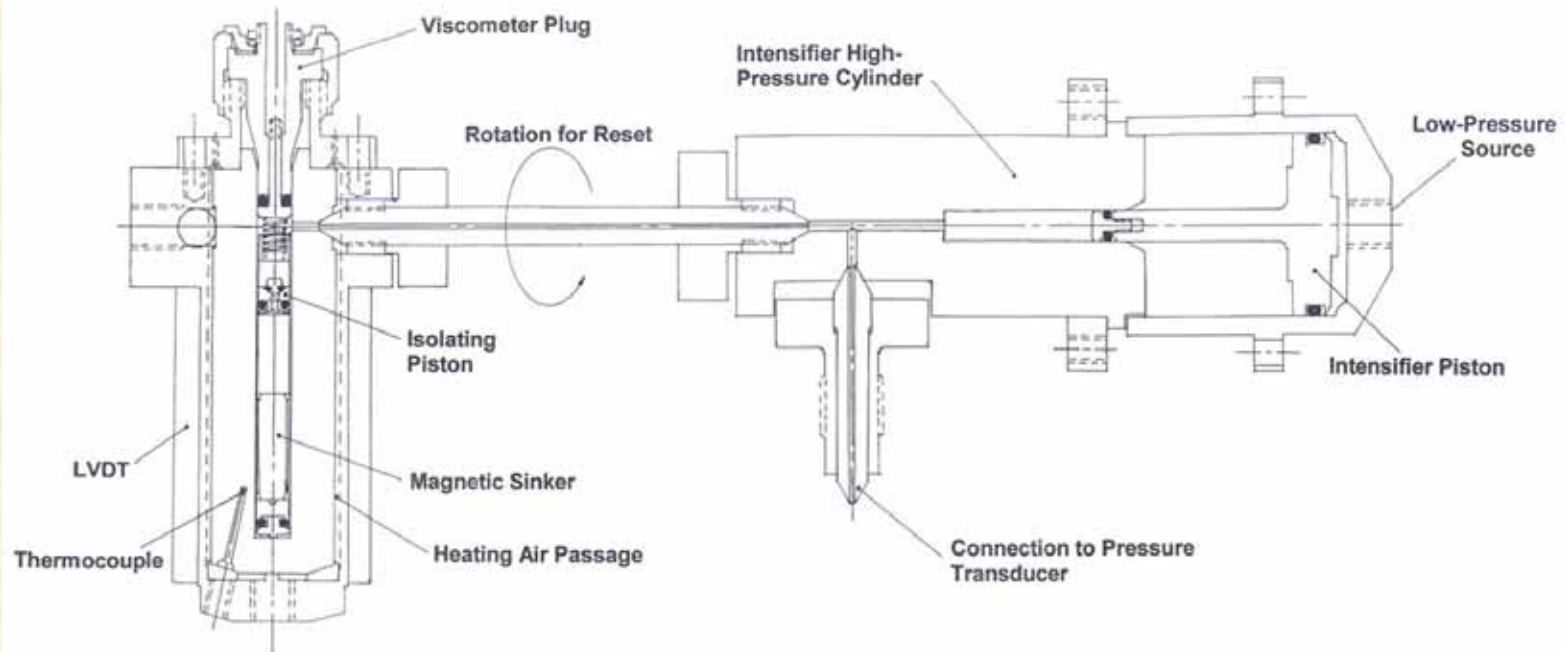
Contest Scoring

- **Quantitative Accuracy Metrics (50%)**
 - At each state point, full credit awarded for predictions within 5% of experimental value
 - Linear interpolation of partial credit awarded for predictions with deviation from experimental result up to 40%
- **Relative Accuracy Metrics (50%)**
 - **Relative Ranking at 0.1MPa (25%)**
 - Compare η/η_{ref} to corresponding expt. ratio
 - reference species selected as candidate with best agreement to experimental result at state point
 - **Relative Viscosity Increase (25%)**
 - $\eta[250MPa]/\eta[0.1Mpa]$ compared to expt.
 - **Similar sliding scale of partial credit applies**

Standard evaluation spreadsheet available at
<http://fluidproperties.org/challenge/third/2006molecule.html>

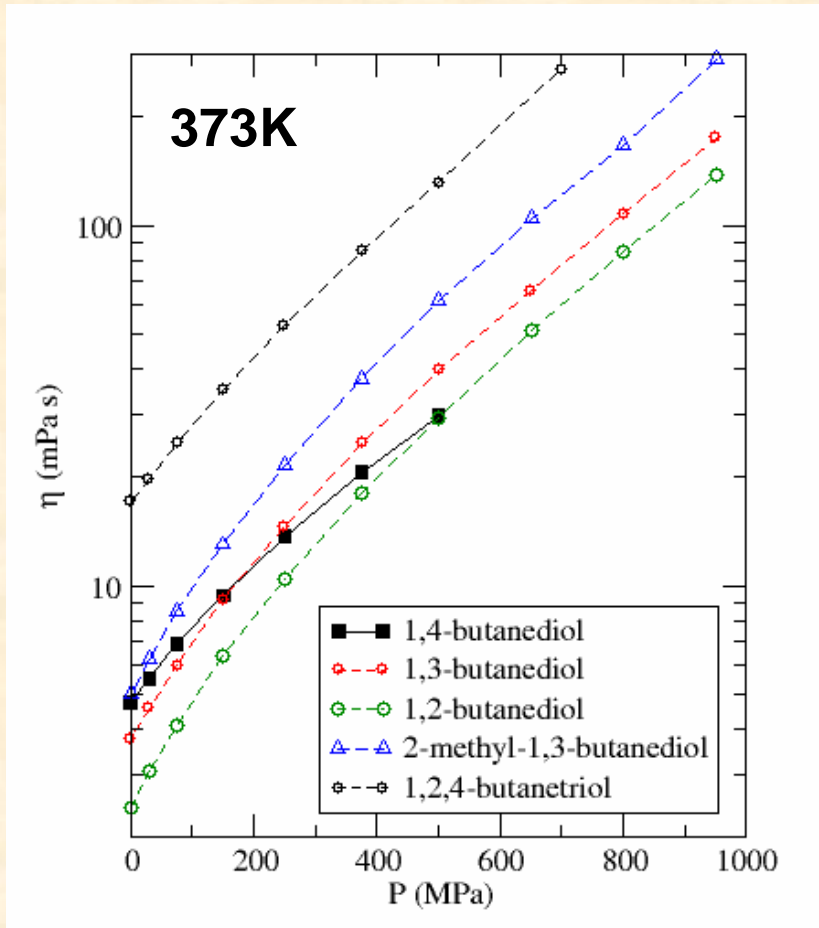
Viscosities – Experimental measurement

- Pressurized falling body viscometer constructed at Georgia Institute of Technology (Scott Bair)
- Dynamic viscosities to within $\pm 3\%$ 25-150C, 0.1 – 1.0GPa

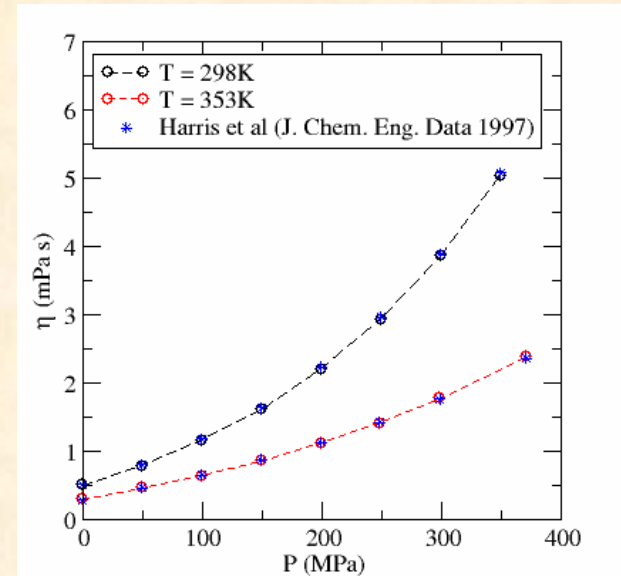


Experimental Results & Validation

Contest molecules isotherms



Viscosity isotherms of n-octane

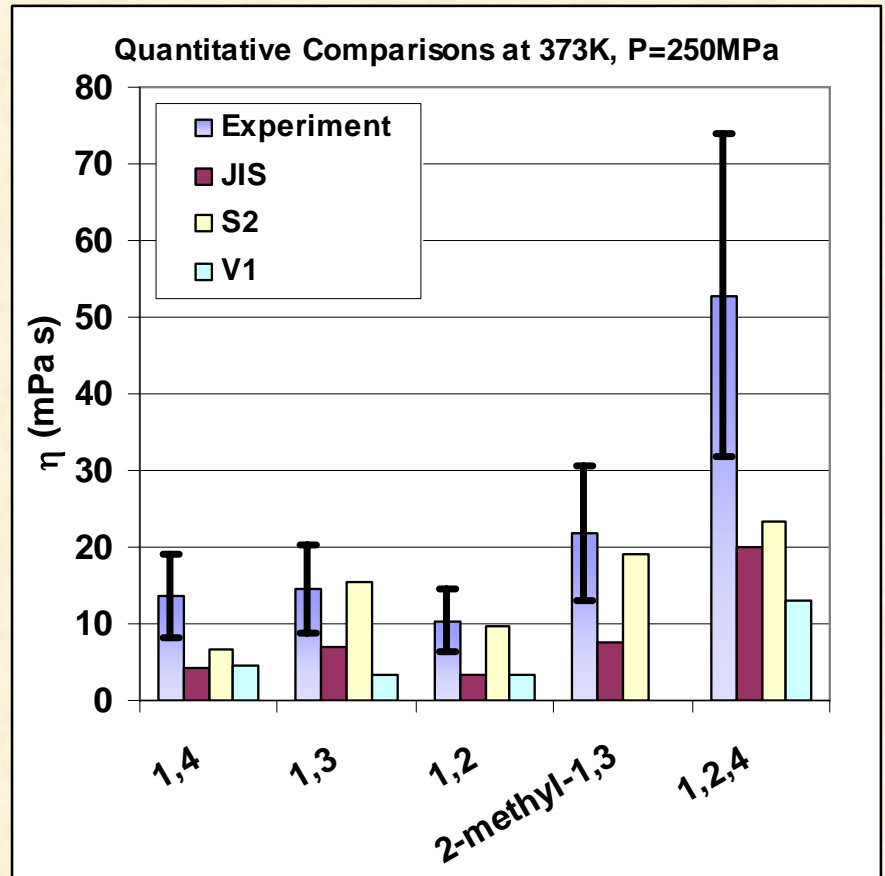
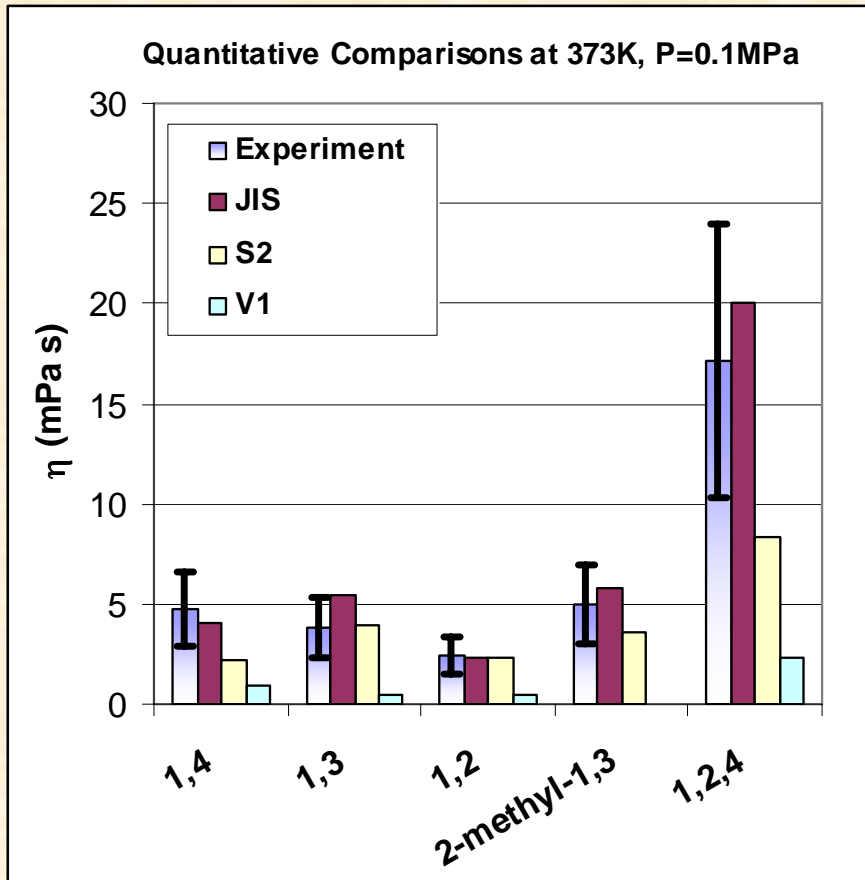


Comparison of 1,4-butanediol viscosities at 0.1 MPa

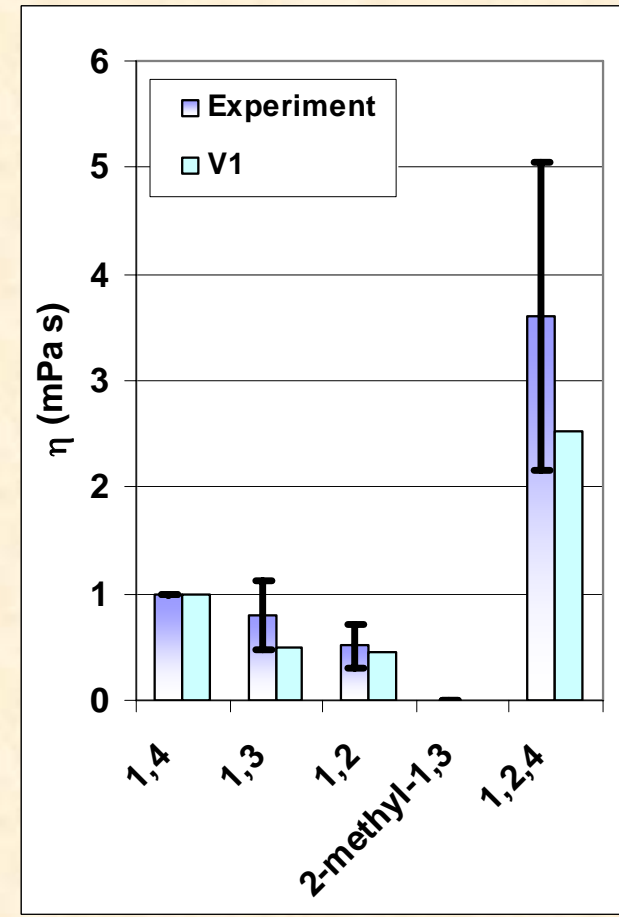
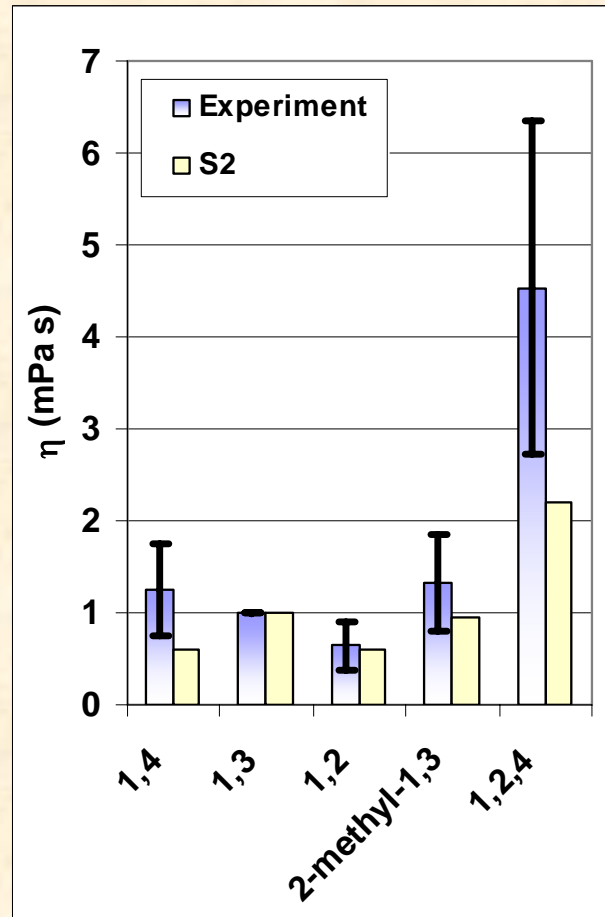
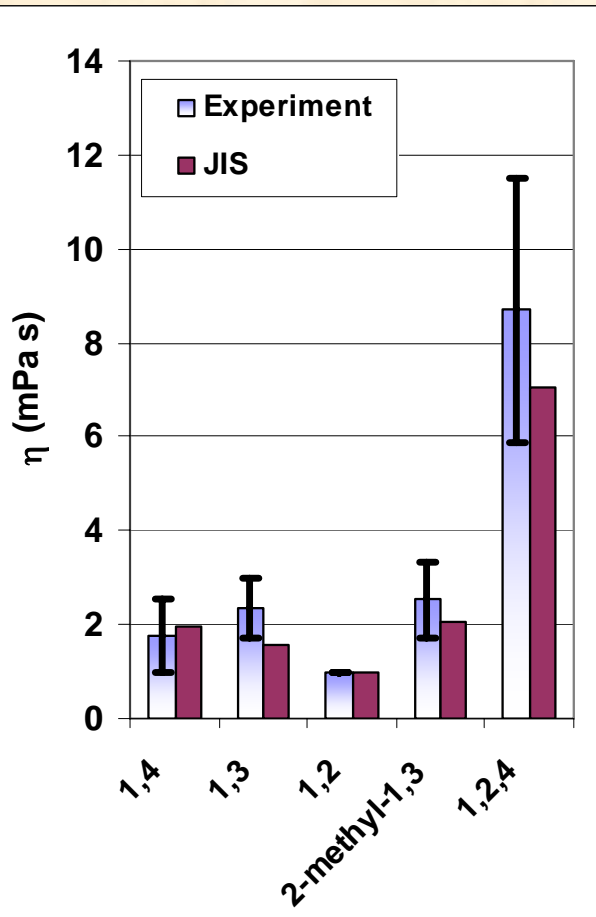
| T K | This work | Lech et al (2001) | Sun et al (1992) | Yang et al (2004) |
|--------|------------|----------------------|---------------------|----------------------|
| | η mPa s | | | |
| 298.15 | 68.1 | 67.0 | 71.1 | 70.6 |
| 312.25 | 36.1 | 35.6 | 37.3 | 37.0 |
| 331.05 | 17.0 | 17.2 | 17.5 | 17.7 |
| 354.65 | 7.87 | 8.22 | 7.99 | 8.21 |
| 373.15 | 4.74 | | 4.76 | |

Full Benchmark report available online at challenge website

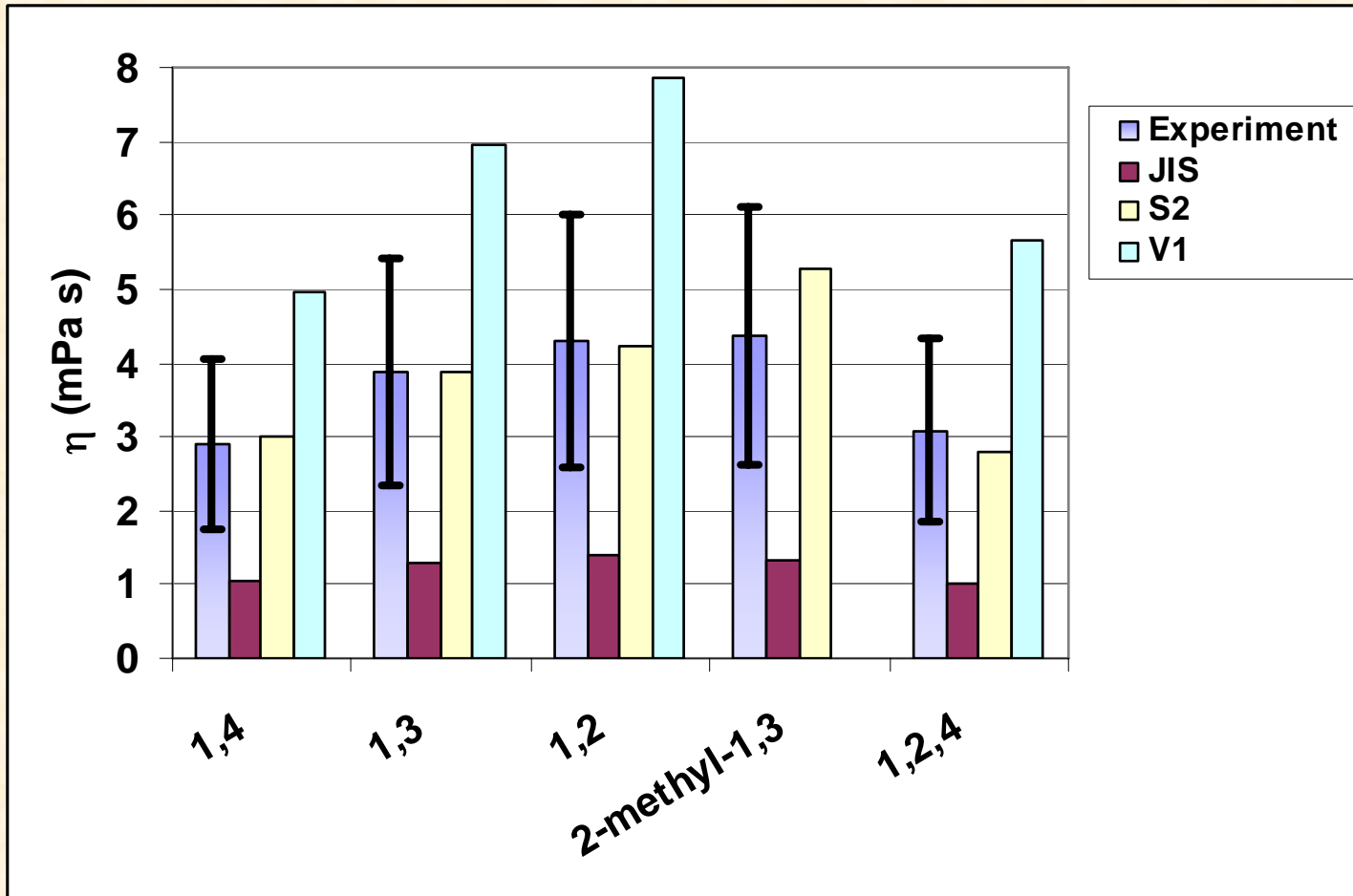
Quantitative Comparisons



Relative Comparisons: 373K, 0.1 MPa



Relative Comparisons: 0.1 \rightarrow 250 MPa



The Winner Is...

L. Zhao, X. Wang, L. Wang, Huai Sun

Shanghai Jiao Tong University

Runner up:

J. L. Rafferty, M. S. Kelkar, J. I. Siepmann and E. J. Maginn

University of Minnesota, University of Notre Dame

