

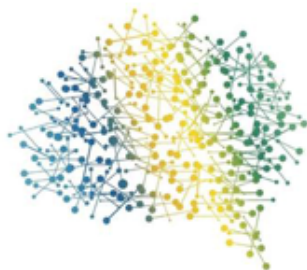
Reproducibility in the Physical Sciences

Joan F. Brennecke

***McKetta Department of Chemical Engineering
University of Texas at Austin***

***Co-Chair of Board on Chemical Science and
Technology***

April 18, 2018

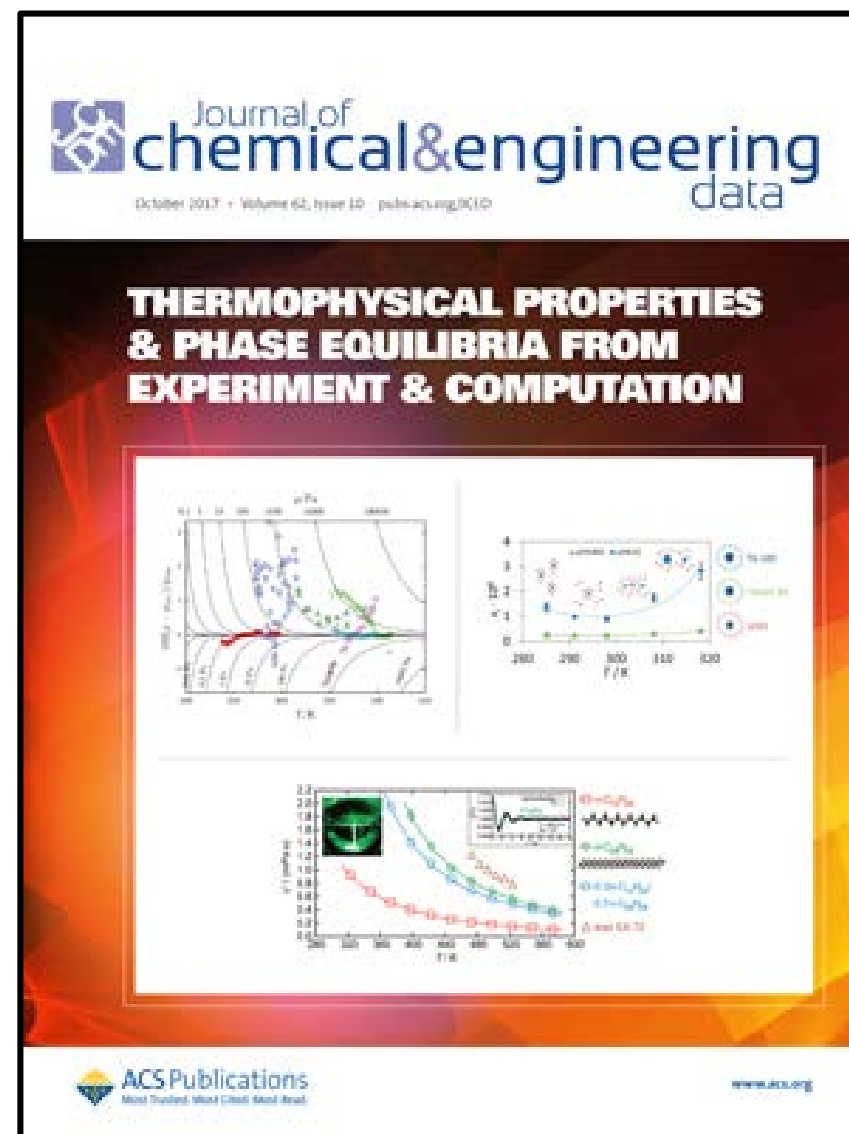


Reproducibility and Replicability in Science

Expertise drawn from experience as

Editor-in-Chief, *Journal of Chemical & Engineering Data*
2010-present

*Views expressed in this presentation are
those of the author and not necessarily
those of the American Chemical Society*



Joint Statement of Editors of Journals Publishing Thermophysical Property Data

Process for Article Submission for *The Journal of Chemical Thermodynamics*, *Fluid Phase Equilibria*, *International Journal of Thermophysics*, *Thermochimica Acta*, and *Journal of Chemical and Engineering Data*

A requirement for submission of a manuscript describing properties is a literature search and comparison of the results with previously reported literature values. Often, reviewers cannot make informed decisions regarding the manuscript because the authors have made only a minimal literature review and comparisons. It is then an unacceptable burden to require reviewers to research previously published literature data to ensure a proper comparison has been made and hence determine the ultimate worth of the manuscript. To accommodate this, a new arrangement has been made with the Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST). Specifically, thermophysical property data for systems reported in a newly submitted manuscript will be compared against the NIST TRC databases. TRC will provide a report to the Editors who at their discretion will forward it to the reviewers and/or the authors. This new procedure is mandatory and will operate by collaborative agreement with Journals in this field including *The Journal of Chemical Thermodynamics*, *Fluid Phase Equilibria*, *International Journal of Thermophysics*, *Thermochimica Acta*, and *Journal of Chemical and Engineering Data*. The Editors will adhere strictly to this policy and there will be no exceptions. This new procedure becomes effective January 2009 and consists of the following elements.

What NIST Does

- **Compares data with data in NIST database**
- **Plots data in various ways to identify anomalous behavior**
- **Checks for reasonable experimental uncertainties**
- Adequate sample characterization, method description, figure and table descriptions

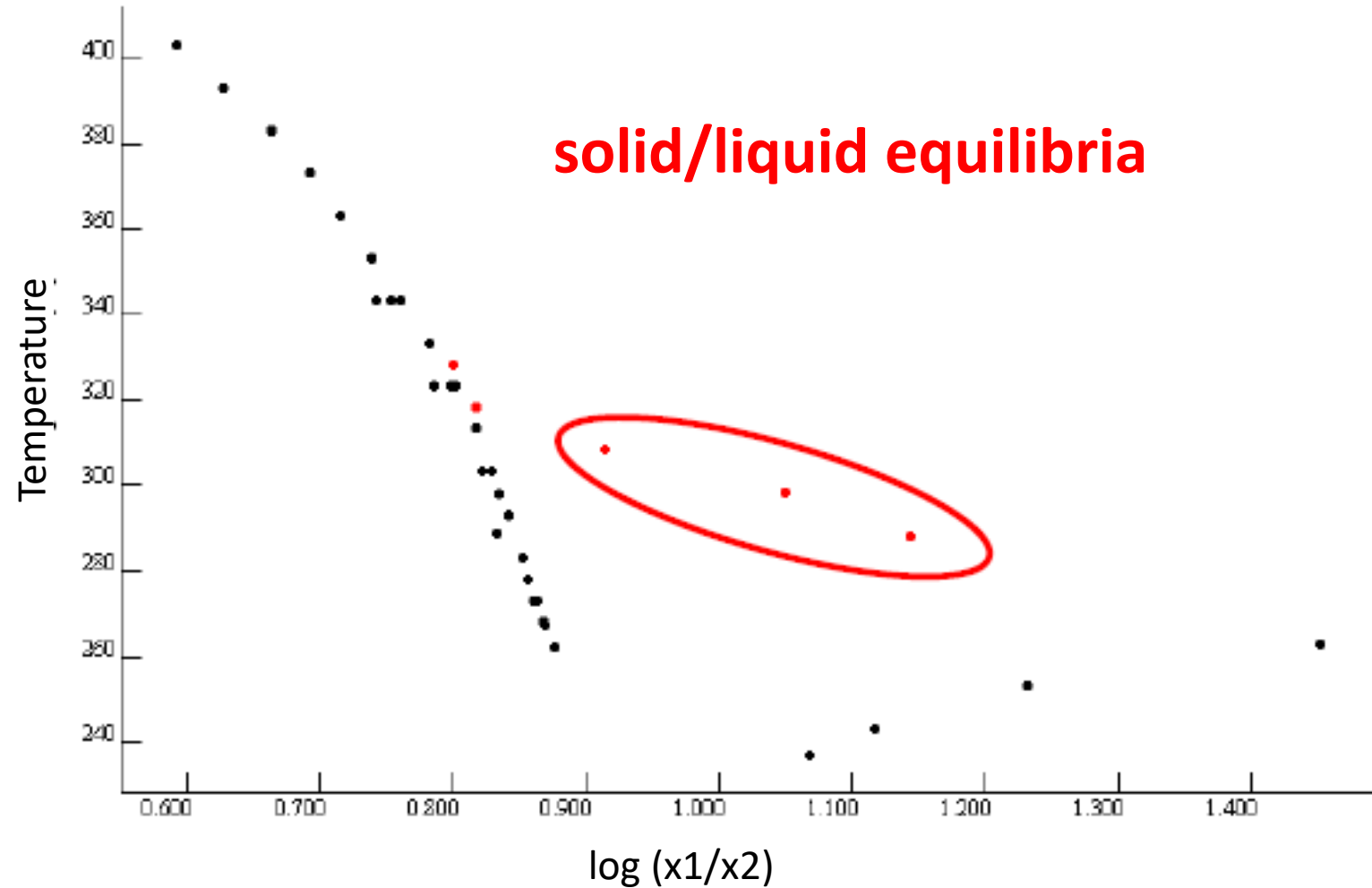
**All prior to manuscripts being accepted for publication,
AFTER revisions in response to external reviewers**

Results of JCED Sample

- 314 recent manuscripts
- 71 (23%) had major issues
- Most* of these reported data inconsistent with the literature or showed unreasonable trends that were not typographical errors
 - Potential outcomes of NIST report:
 - Authors remeasured and corrected
 - Those data removed from manuscript
 - Manuscript rejected by Editors

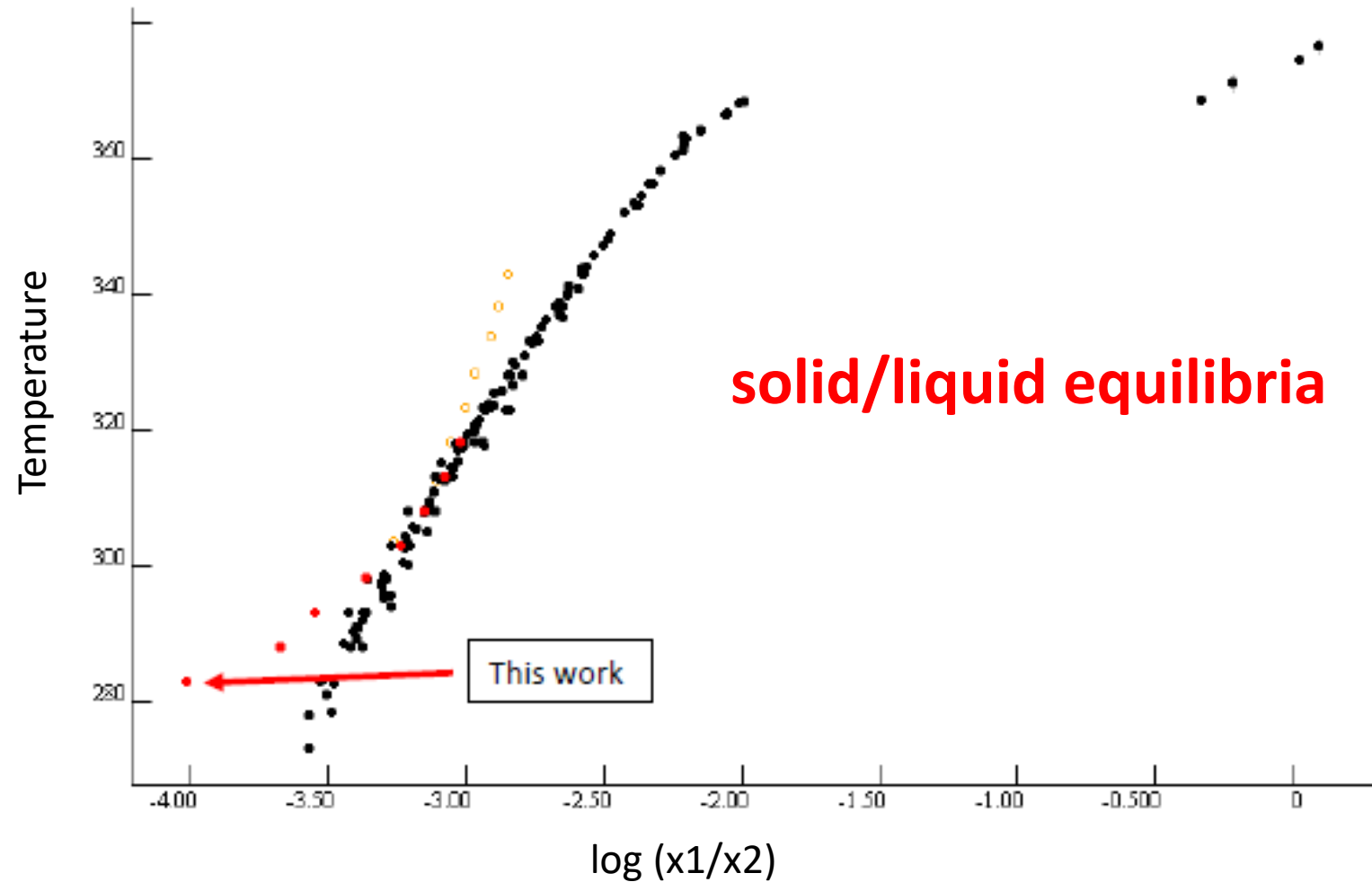
* 65-75%

Does Not Match Literature



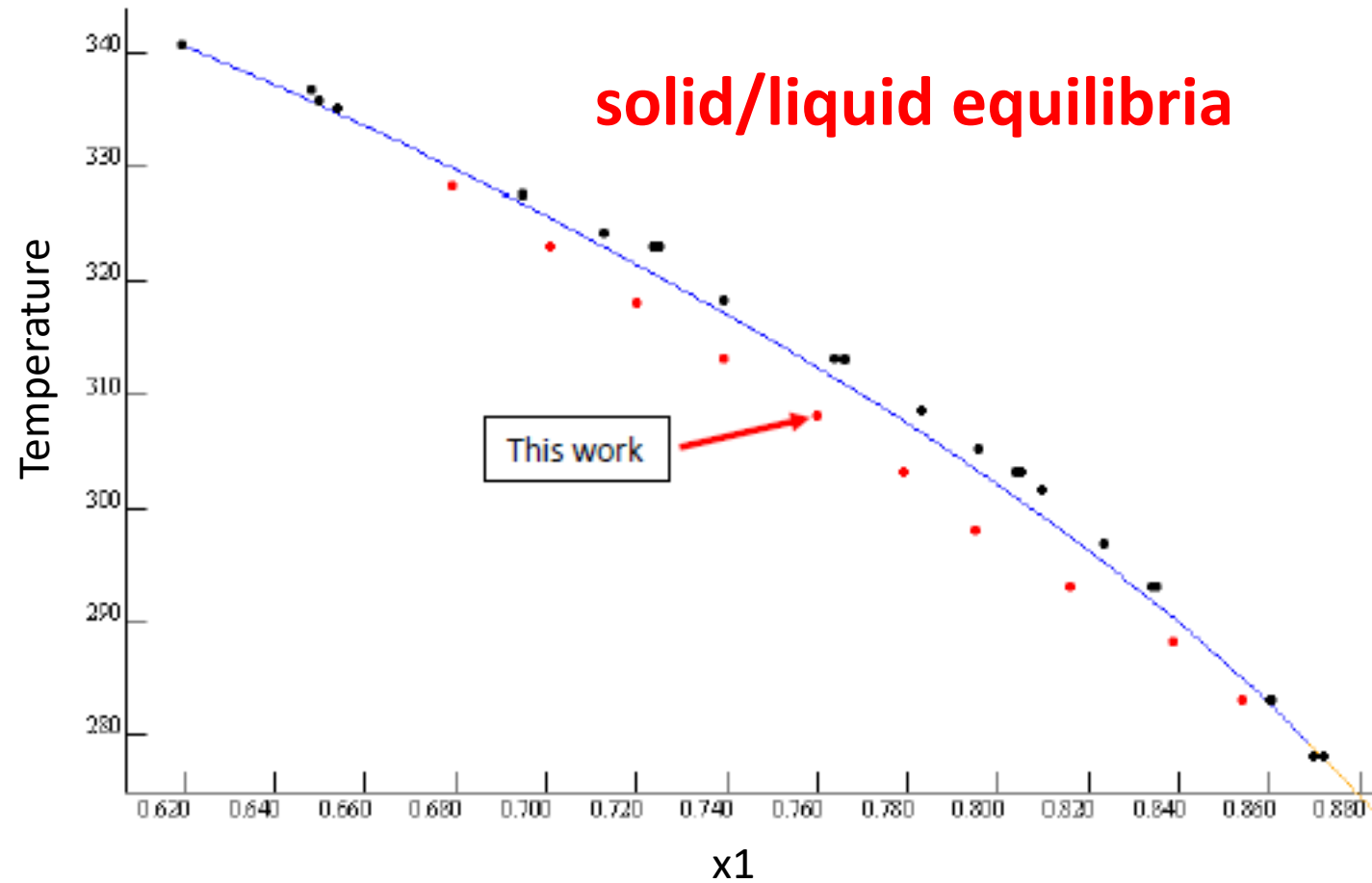
Example 1

Does Not Match Literature



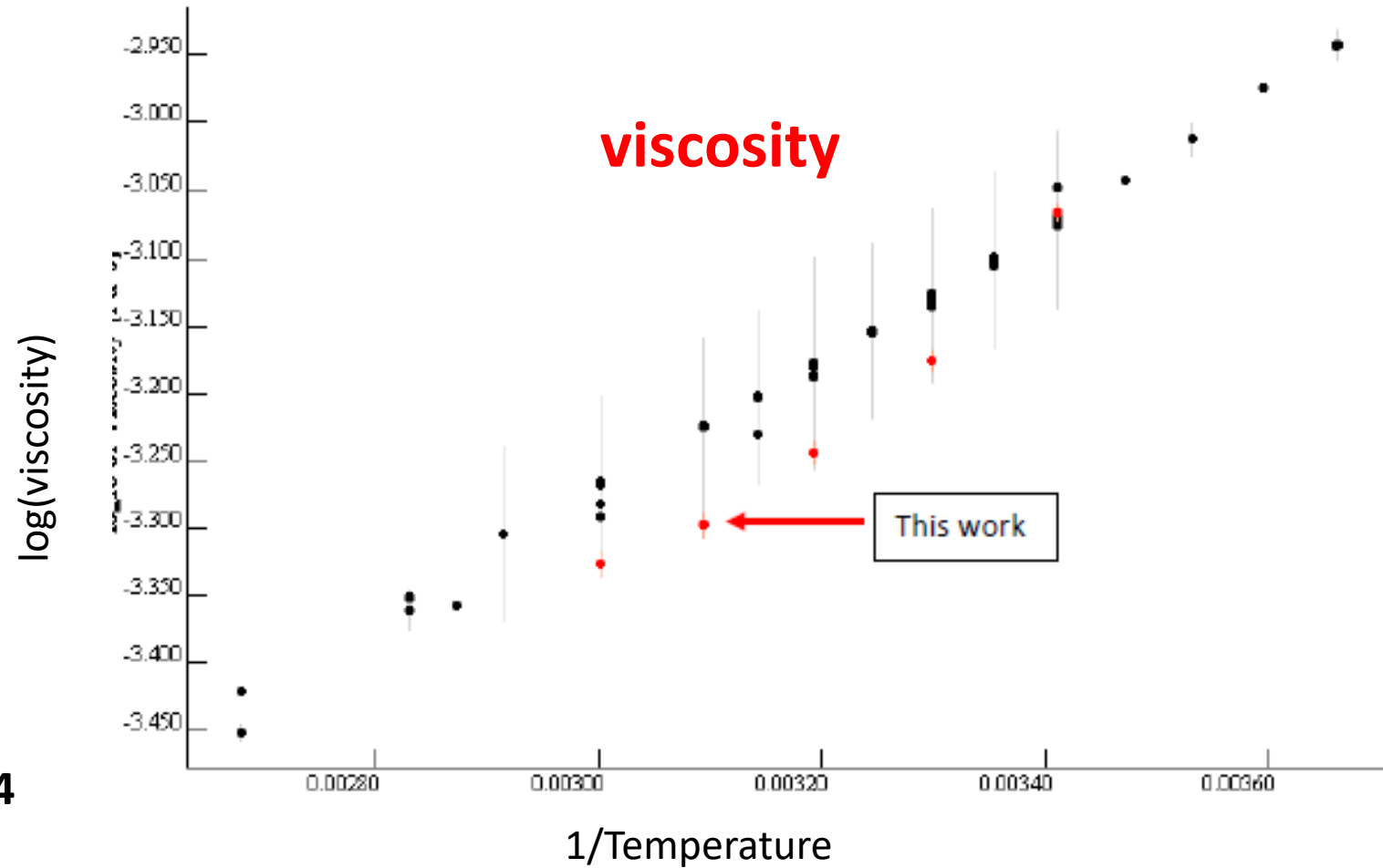
Example 2

Does Not Match Literature



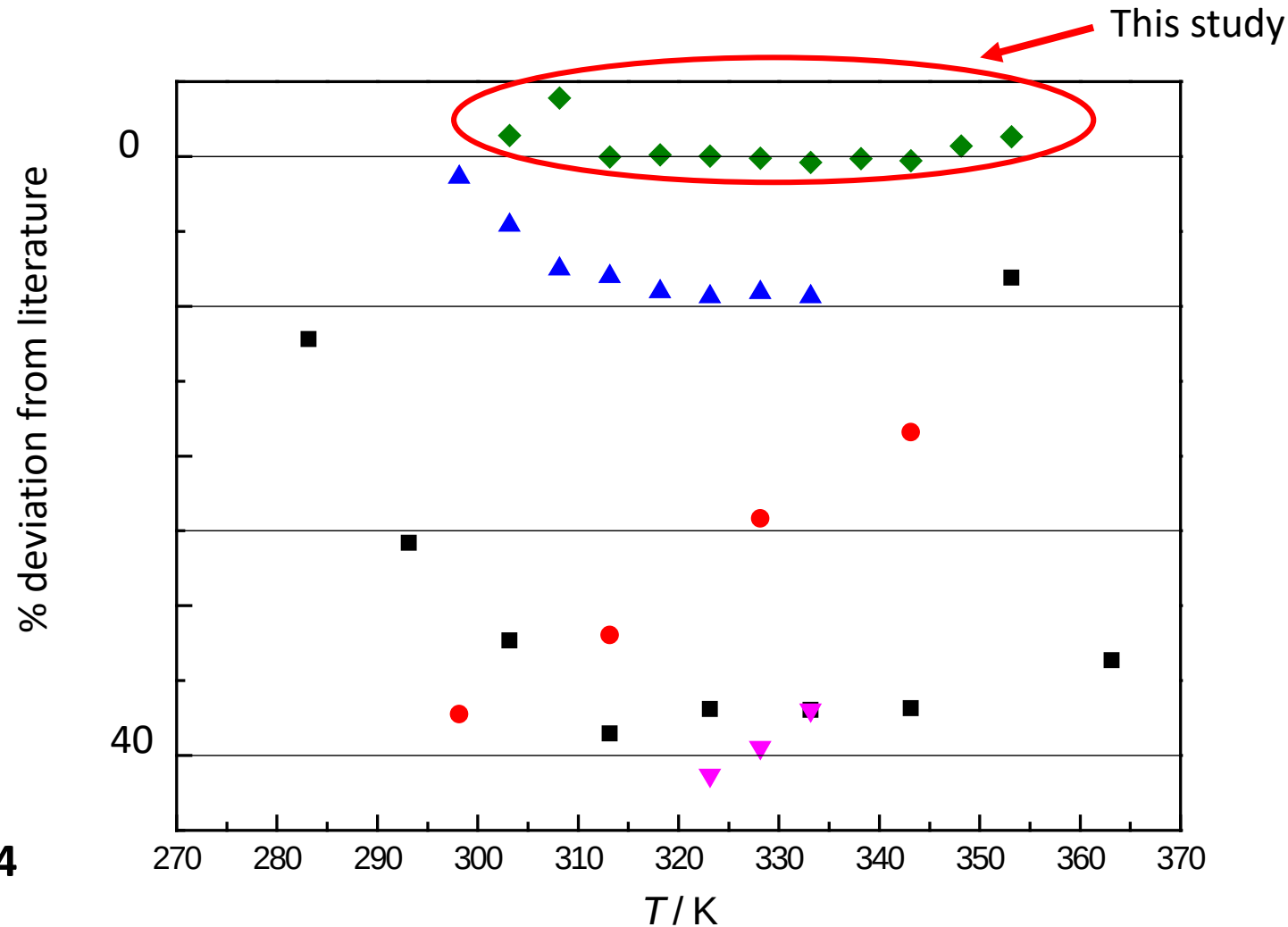
Example 3

Does Not Match Literature



Example 4

Does Not Match Literature

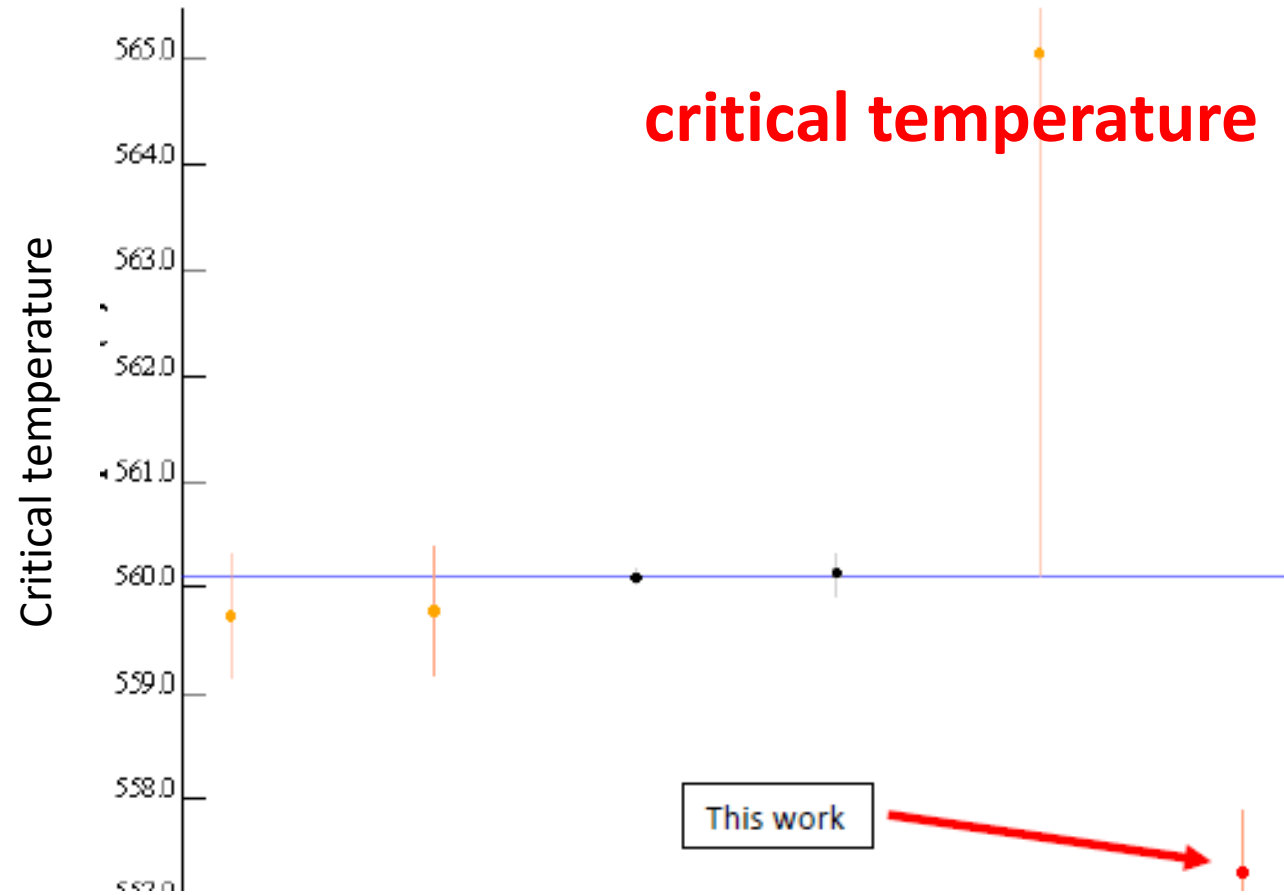


viscosity

Ionic liquid; hygroscopic;
water content not always
reported
Water reduces viscosity

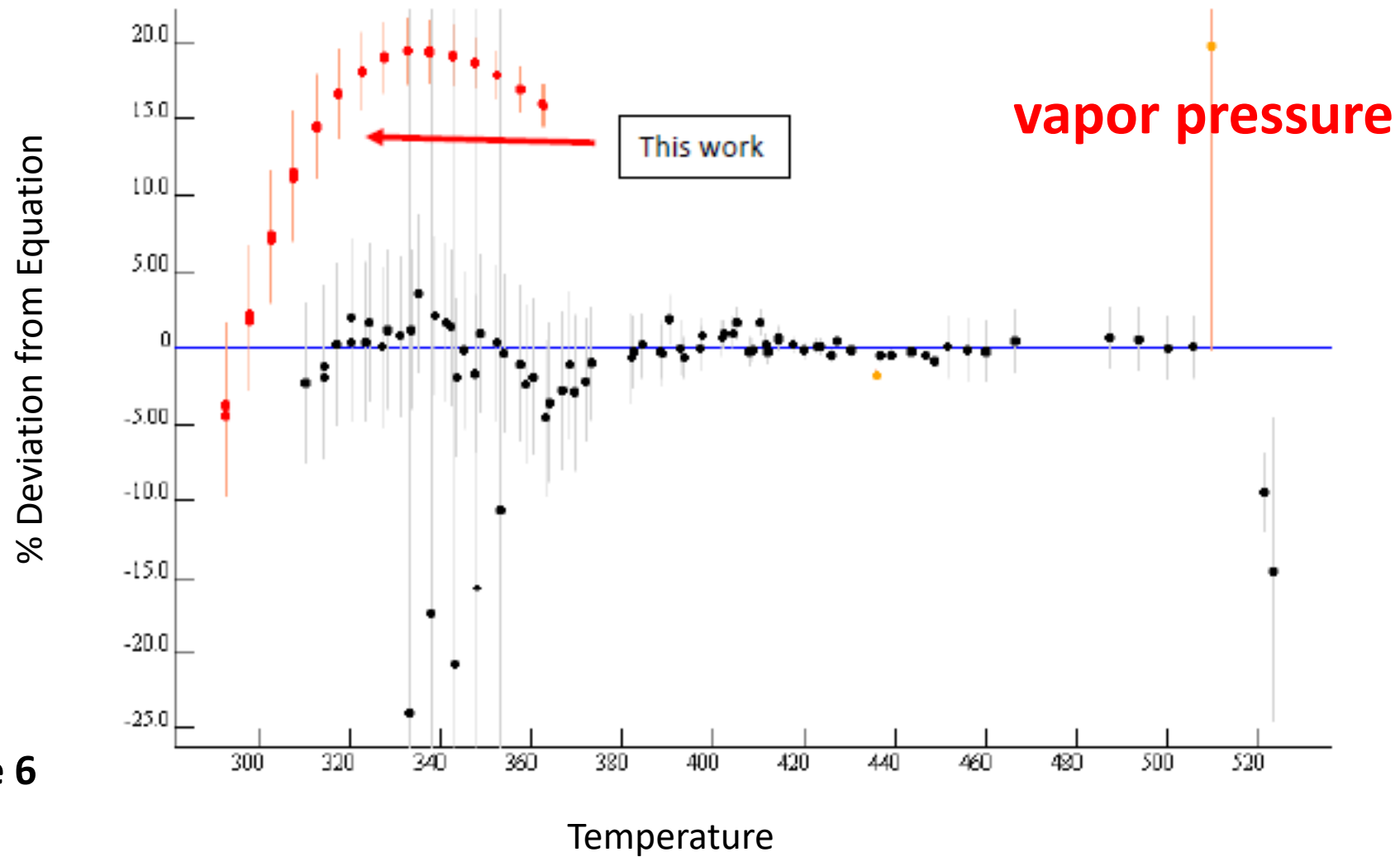
Example 4

Does Not Match Literature



Example 5

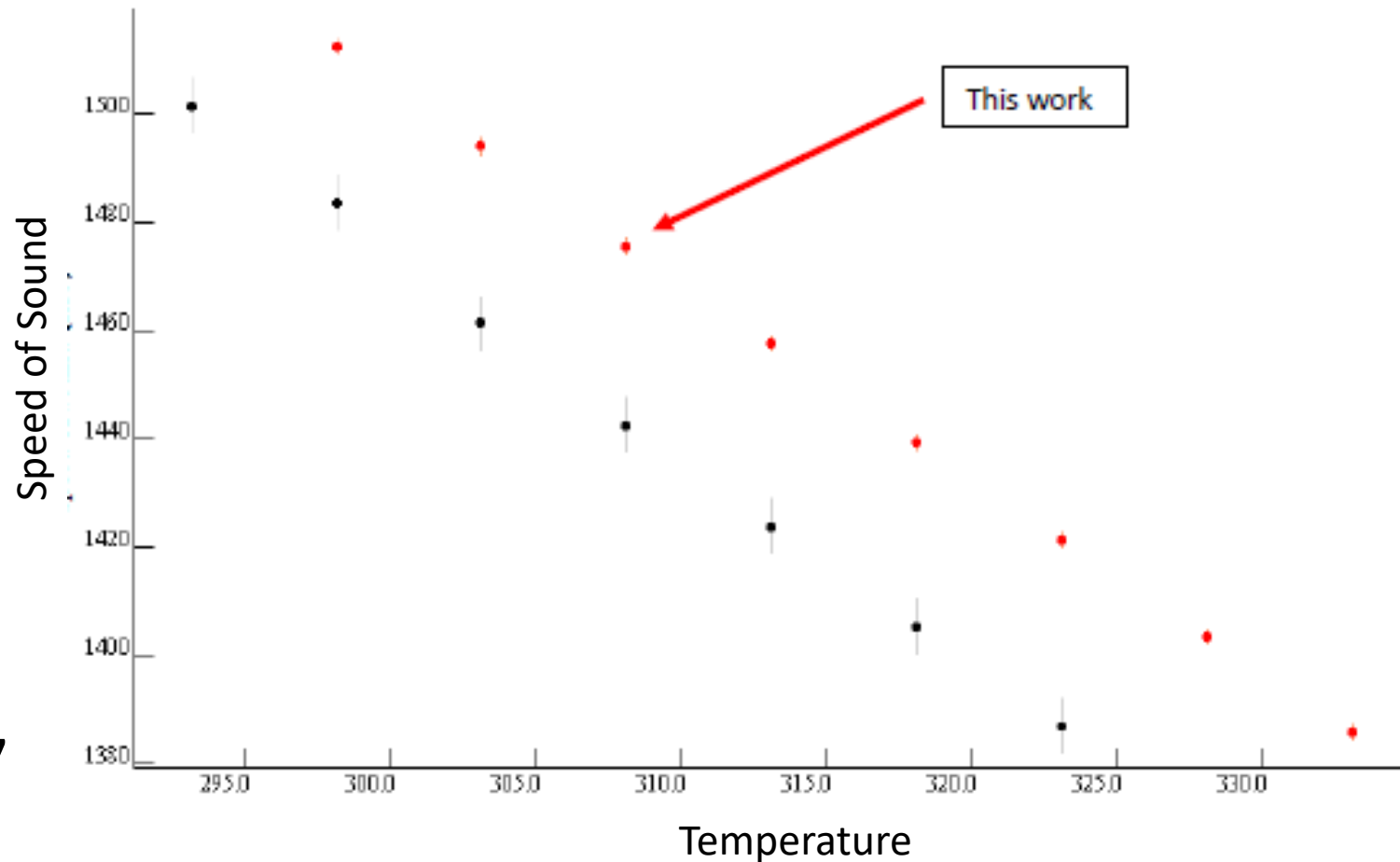
Does Not Match Literature



Example 6

Does Not Match Literature

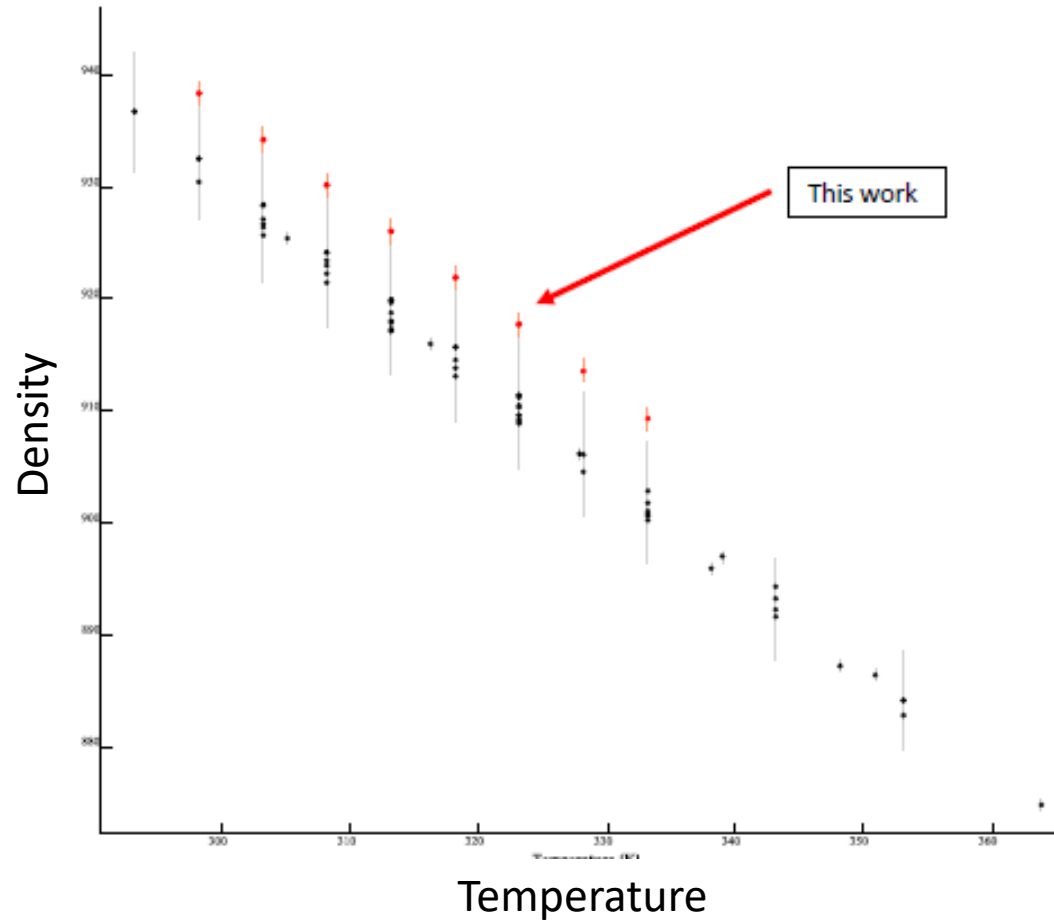
Uncertainties too small



Example 7

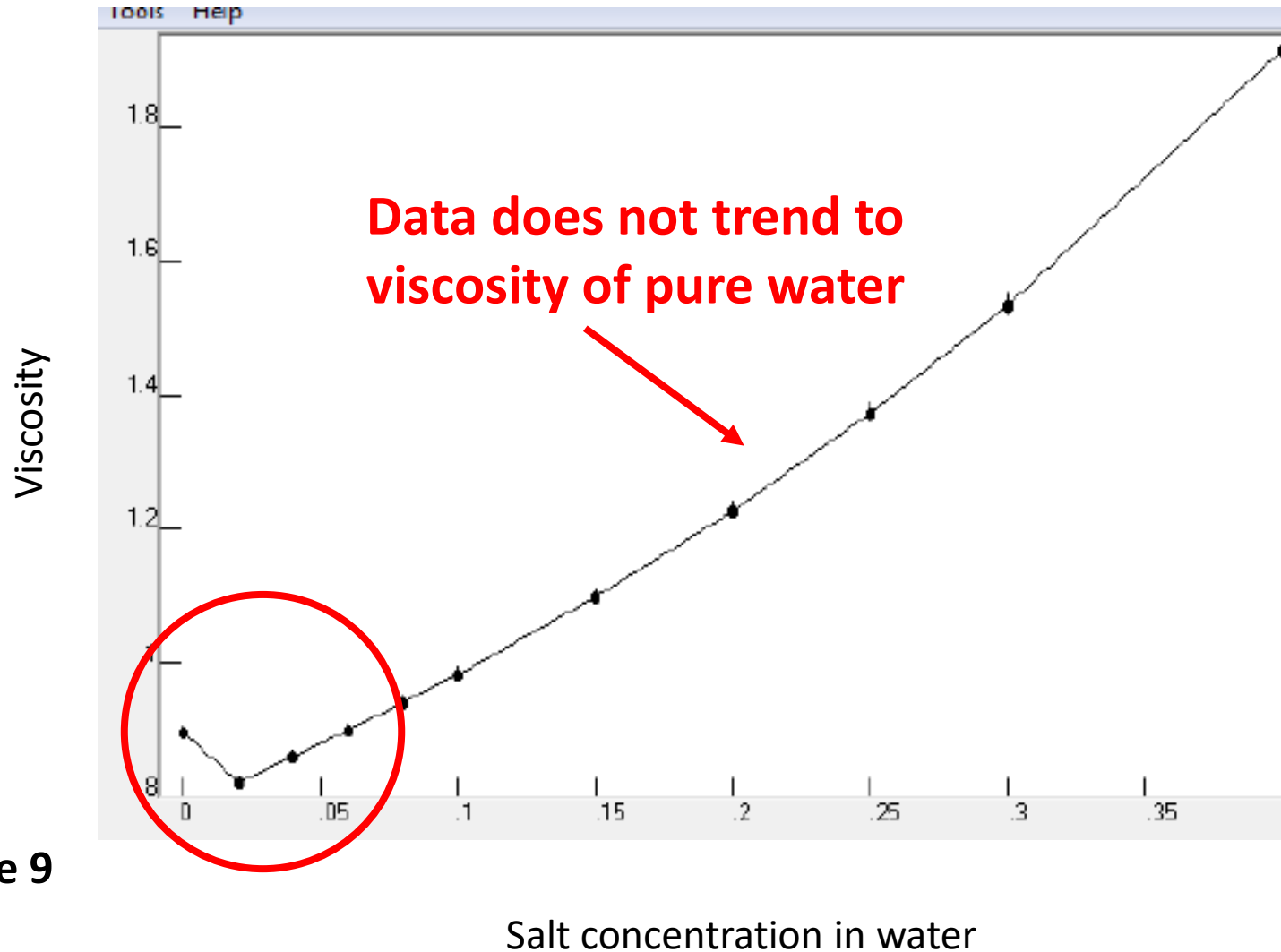
Does Not Match Literature

Uncertainties too small



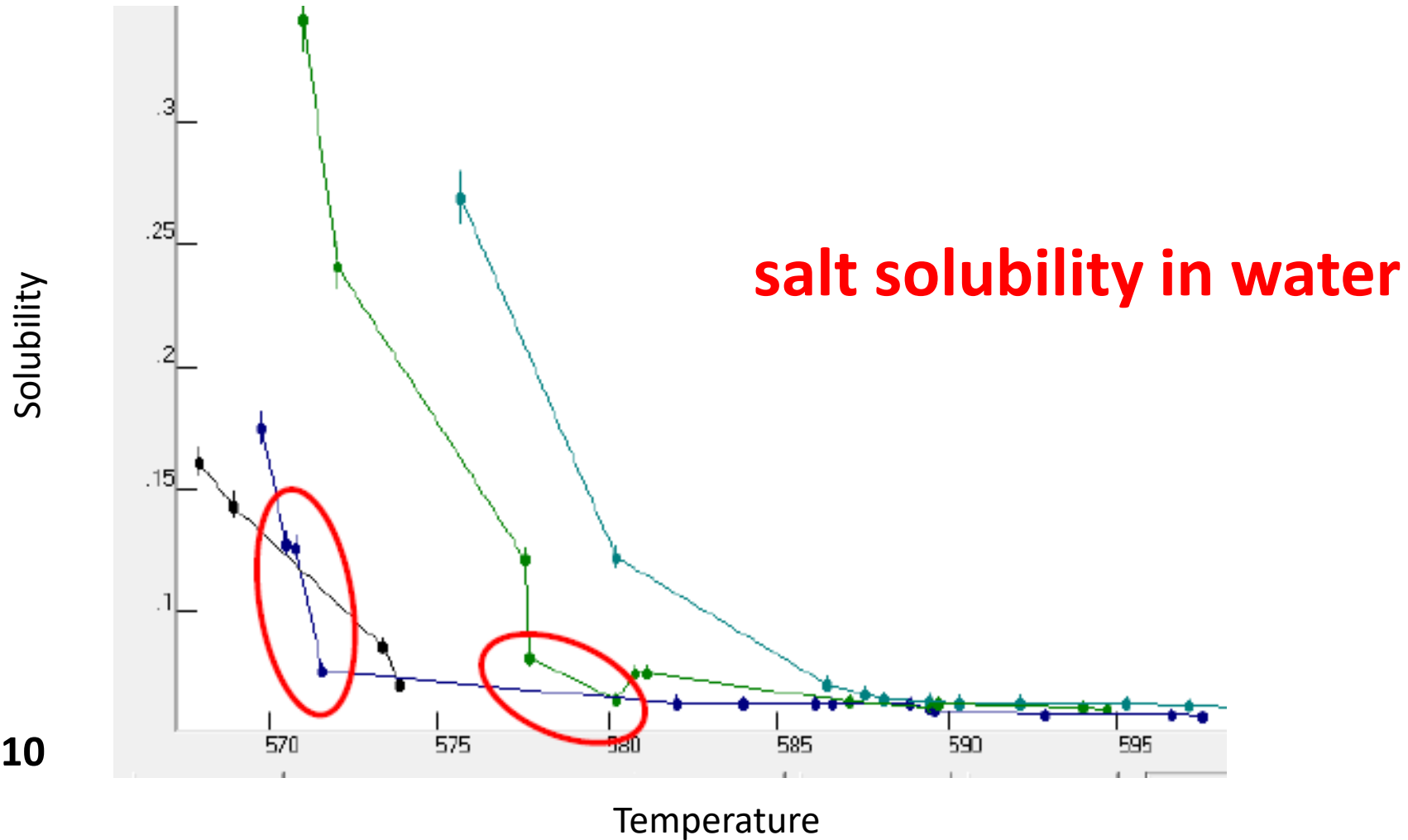
Example 8

Unreasonable Values or Trends



Example 9

Unreasonable Values or Trends



Example 10

Conclusions from JCED Sample

- Much of what I showed would have made it into the archival literature if it hadn't been for the NIST data checking
- Reproducibility is a problem for authors submitting thermophysical properties and phase equilibria data to JCED
- Is this a more general problem?

I would argue “Yes”

See following examples from other journals

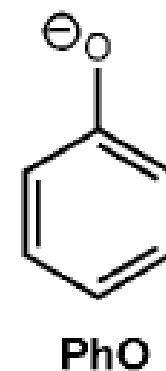
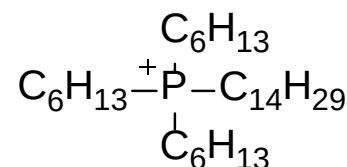
Tuning the Basicity of Ionic Liquids for Equimolar CO₂ Capture**

Congmin Wang,* Xiaoyan Luo, Huimin Luo, De-en Jiang, Haoran Li, and Sheng Dai*

Table 1: The effect of anion pK_a on the stability, absorption capacity, and absorption enthalpy.^[a]

Ionic liquid	T _{dec} [°C]	Absorption capacity ^[b]	Absorption enthalpy ^[c]	pK _a in DMSO ^[d]
[P ₆₆₆₁₄][Pyr]	182	1.02	91.0	19.8
[P ₆₆₆₁₄][Im]	252	1.00	89.9	18.6 (14.5)
[P ₆₆₆₁₄][Ind]	277	0.98	63.1	17.8
[P ₆₆₆₁₄][Triz]	310	0.95	56.4	13.9
[P ₆₆₆₁₄][Bentriz]	332	0.17	37.2	11.9
[P ₆₆₆₁₄][Tetz]	340	0.08	19.1	8.2
[P ₆₆₆₁₄][Oxa]	224	0.91	69.8	(12.5)
[P ₆₆₆₁₄][PhO]	263	0.50	46.7	(10.0)

[a] The absorption was carried out at 23 °C for 20 min. [b] Mol CO₂ per mol IL. [c] Calculated values based on B3LYP/6-31++G(p,d) method. [d] Values given in brackets are in H₂O.



Tuning the Physicochemical Properties of Diverse Phenolic Ionic Liquids for Equimolar CO₂ Capture by the Substituent on the Anion

Congmin Wang,^{*[a, b]} Huimin Luo,^[d] Haoran Li,^[a] Xiang Zhu,^[c] Bo Yu,^[d] and Sheng Dai^{*[b, c]}

Ionic liquid	<i>t</i> [min] ^[a]	CO ₂ absorption ^[b]
[P ₆₆₆₁₄][4-Me-PhO]	30	0.91
[P ₆₆₆₁₄][4-MeO-PhO]	30	0.92
[P ₆₆₆₁₄][4-H-PhO]	30	0.85
[P ₆₆₆₁₄][4-Cl-PhO]	30	0.82
[P ₆₆₆₁₄][4-CF ₃ -PhO]	30	0.61
[P ₆₆₆₁₄][4-NO ₂ -PhO]	20	0.30

[a] Determined at 30 °C. [b] Mole CO₂ per mole of ionic liquid.



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DOI: 10.1039/c4cc06944g

www.rsc.org/chemcomm

Highly efficient CO₂ capture by carbonyl-containing ionic liquids through Lewis acid–base and cooperative C–H...O hydrogen bonding interaction strengthened by the anion†

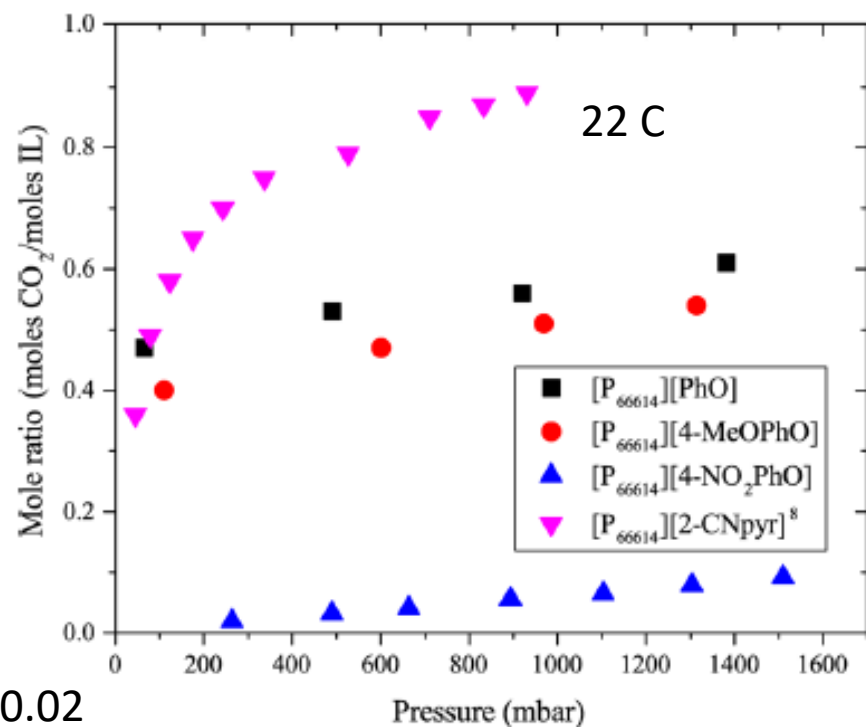
Fang Ding,^a Xi He,^a Xiaoyan Luo,^a Wenjun Lin,^a Kaihong Chen,^a Haoran Li^{ab} and Congmin Wang^{*a}

Anions	Absorption capacities ^a	$\Delta H^{b,c}$
[PhO]	0.81	—
[4-Kt-PhO]	1.04	−13.9
[4-EF-PhO]	1.03	−13.5
[4-CHO-PhO]	1.01	−17.6
[Im]	0.98	—
[4-CHO-Im]	1.24	−18.9
[Im-EA] ^d	0.06	−2.7
[4,5-2EF-Im]	0.85	−14.4

^a Reaction conditions: CO₂ absorbed at 30 °C and 1 bar, mole CO₂ per mole IL. ^b The interaction enthalpies of the complexes of carbonyl-based groups and CO₂, kJ mol^{−1}. ^c Carried out at the B3LYP/6-31++G(d,p) level. ^d Carbonyl-based cation.

DOI: 10.1021/acs.jpcb.5b06934
J. Phys. Chem. B 2016, 120, 1509–1517

CO₂ Chemistry of Phenolate-Based Ionic Liquids

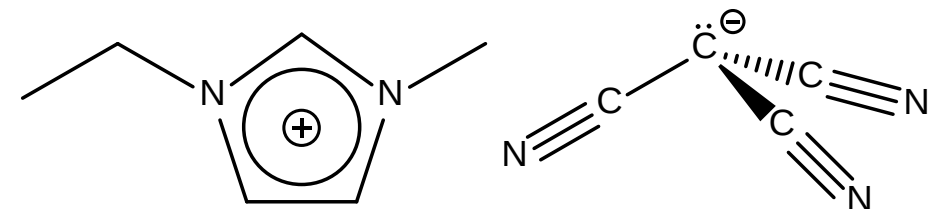
Tae Bum Lee,[†] Seungmin Oh,[†] Thomas R. Gohndrone,[†] Oscar Morales-Collazo,[†] Samuel Seo,[†]
Joan F. Brennecke,*[†] and William F. Schneider*^{†,‡}

+/-0.02

CO₂ uptake @ 20-30 °C and 0.9-1 bar

Us	Wang et al
0.56	0.50 or 0.85 or 0.81
0.51	0.92
0.06	0.30

Liquid-Liquid Equilibrium



1-ethyl-3-methyl-imidazolium Tricyanomethanide

Ionic Liquid (IL) + Toluene

L1 = mostly toluene

L2 = rich in IL but lots of toluene in it

Ionic Liquid (IL) + Heptane

L1 = mostly heptane

L2 = rich in IL but a little bit of heptane in it

Liquid-Liquid Equilibrium

Toluene Solubility in 1-ethyl-3-methyl-imidazolium Tricyanomethanide

Source	Temperature	mol% Toluene	Analytical Method
Literature ¹	40°C	65.45 %	Multiple Headspace Extraction
Our Work	40°C	48.7 %	GC with Internal Standard
Our Work	40°C	50.2 %	H ¹ NMR
Our Work	25°C	49.7 %	GC with Internal Standard
Our Work	25°C	50.7 %	H ¹ NMR

Heptane Solubility in 1-ethyl-3-methyl-imidazolium Tricyanomethanide

Source	Temperature	mol% Heptane	Analytical Method
Literature ¹	40°C	0.91 %	Multiple Headspace Extraction
Our Work	40°C	0.74 %	GC with Internal Standard

(1) Larriba, M.; Navarro, P.; García, J.; Rodríguez, F. Liquid-Liquid Extraction of Toluene from Heptane Using [emim][DCA], [bmim][DCA], and [emim][TCM] Ionic Liquids. *Ind. Eng. Chem. Res.* **2013**, 52 (7), 2714–2720.

Summary

- Reproducibility **IS** an issue in the physical sciences
- What is the problem?
 - Laziness and sloppiness
 - Publication pressures and misguided reward structures
 - This is not likely intentional fraud
- Joint programs like one with NIST Thermodynamics Research Center are absolutely invaluable to the sciences
 - Applicable portions of other ACS journals considering if NIST has bandwidth