



Aalborg Universitet

AALBORG UNIVERSITY
DENMARK

Determining the liquidus viscosity of glass-forming liquids through differential scanning calorimetry

Zheng, Q.J.; Zheng, J.F. ; Solvang, M.; Yue, Yuanzheng; Mauro, J.C.

Published in:
Journal of the American Ceramic Society

DOI (link to publication from Publisher):
[10.1111/jace.17363](https://doi.org/10.1111/jace.17363)

Creative Commons License
CC BY-NC 4.0

Publication date:
2020

Document Version
Accepted author manuscript, peer reviewed version

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Zheng, Q. J., Zheng, J. F., Solvang, M., Yue, Y., & Mauro, J. C. (2020). Determining the liquidus viscosity of glass-forming liquids through differential scanning calorimetry. *Journal of the American Ceramic Society*, 103(11), 6070–6074. <https://doi.org/10.1111/jace.17363>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal -

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.



PROFESSOR YUANZHENG YUE (Orcid ID : 0000-0002-6048-5236)

DR JOHN C. MAURO (Orcid ID : 0000-0002-4319-3530)

Article type : Rapid Communication

Determining the liquidus viscosity of glass-forming liquids through differential scanning calorimetry

Qiuju Zheng^{1,†}, Jinfeng Zheng^{1,†}, Mette Solvang², Yuanzheng Yue³, John C. Mauro^{4,*}

¹School of Materials Science and Engineering, Qilu University of Technology, Jinan, China

²Rockwool International A/S, 2640 Hedehusene, Denmark

³Department of Chemistry and Bioscience, Aalborg University, DK-9000 Aalborg, Denmark

⁴Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, USA

[†]These authors contribute equally to the paper.

*Corresponding author: jcm426@psu.edu

Abstract

Viscosity at the liquidus temperature (T_L), η_L , is a critical parameter for the design of new glasses, particularly for industrial glass production where crystallization must be suppressed. However, a direct viscometric determination of η_L for a glass-forming system is difficult due to crystallization. Here we propose an alternative approach for determining η_L through differential scanning calorimetry

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1111/JACE.17363](https://doi.org/10.1111/JACE.17363)

This article is protected by copyright. All rights reserved

(DSC). Specifically, DSC is used to measure both the viscosity curve and liquidus temperature of a glass-forming system and then derive its η_L value. The η_L values determined using DSC are found to be in excellent agreement with those measured through viscometry. The DSC approach is applicable to various glass-forming systems covering a wide range of fragilities and η_L values spanning over five orders of magnitude. Other advantages of this approach are its accuracy and small sample requirements.

Keywords: Liquidus temperature; Viscosity; Liquidus viscosity; Fragility, Differential scanning calorimetry

1. Introduction

Liquidus viscosity (η_L) is defined as the shear viscosity of a glass-forming liquid at its liquidus temperature (T_L) and is a critical parameter in glass science and technology.¹ In industrial glass production, η_L affects the ability to manufacture the glass, i.e., glass workability while avoiding crystallization during melting or forming processes. Liquidus viscosity is an especially useful parameter since it incorporates both the thermodynamic (T_L) and kinetic (η) aspects of crystallization in a single parameter. Liquid viscosity is thus a measure of glass-forming ability, which is also correlated to glass stability.^{2,3} A larger η_L indicates a higher glass-forming ability. Hence, η_L is a governing factor for glass fiberizing processes,⁴ and it is important in the design of new industrial glass compositions. For example, recently a fiber spinnability index has been proposed to quantify the ability of a glass melt to be spun into fiber filament in terms of η_L .⁴

Liquidus viscosity is typically determined by direct viscosity measurements at T_L . Viscosity measurements can be performed with various types of viscometers,⁵ but several factors can make it difficult to apply viscometry in many cases, e.g., melt volatilization, crystallization, limited sample availability. Zheng et al. proposed an alternative method to calculate viscosity by performing DSC measurements.⁶ Viscosity can be described by three-parameter viscosity models, among which MYEGA is the most accurate⁷:

$$\log_{10} \eta(T) = \log_{10} \eta_{\infty} + (12 - \log_{10} \eta_{\infty}) \frac{T_g}{T} \exp \left[\left(\frac{m}{12 - \log_{10} \eta_{\infty}} - 1 \right) \left(\frac{T_g}{T} - 1 \right) \right] \quad (1)$$

Since the high-temperature viscosity limit, $\eta_{\infty}(x)$ (where x is composition), has been demonstrated to be a constant $10^{-2.93}$ Pa·s,⁸ once glass transition temperature $T_g(x)$ ($\eta(T_g(x), x) = 10^{12}$ Pa·s) and fragility index $m(x)$ are determined, the entire viscosity curve can be obtained. The fragility index (m_{vis}) describes the rate of viscosity change of a glass-forming liquid with temperature at T_g .⁹ The definition is

$$m(x) = \left. \frac{\partial \log_{10} \eta(T, x)}{\partial (T_g(x)/T)} \right|_{T=T_g(x)} \quad (2)$$

Zheng et al. have introduced a model to calculate m_{vis} based on measurement of the calorimetric fragility index (m_{DSC}), i.e., the changing rate of fictive temperature (T_f) with heating (cooling) rate in a small T_f range around T_g .⁶ The fictive temperature, T_f , is defined as the temperature at which the

configurational enthalpy of the glass equals that of the corresponding liquid state.¹⁰ The calorimetric glass transition temperature ($T_{g,DSC}$) can be used as the kinetic glass transition temperature ($T_{g,vis}$). The method works well for different glass families covering a wide range of liquid fragilities.⁶

Liquidus temperature, T_L , is defined as the highest temperature at which crystals are in equilibrium in a system, which is inherently a thermodynamic quantity.² Various methods have been applied to determine T_L in glass science and in the glass industry. The traditional method to measure T_L of glass-forming compositions is based on holding the sample for a prolonged period of time in a gradient furnace. This method is time consuming, and the determined T_L value depends on the accuracy of the furnace temperature and the resolution limit of the microscopic analyses.⁴ Another method for determining T_L is based on DSC measurements. The offset point of the DSC melting peak is regarded as the temperature at which the last crystal vanishes (examples can be found in Fig. 1). However, the DSC T_L value is dynamic, shifting to higher temperature with increasing DSC heating rate (q). Ferreira et al. have proposed the equilibrium T_L value can be obtained by extrapolating the T_L - q relation to $q = 0$ K/min (as illustrated in Fig. 2).^{2,11} The effect of the heating rate on T_L has been eliminated in this way, and the dynamic T_L is converted to thermodynamic T_L . This valuable method is applicable to both simple and multicomponent glasses.

Here we propose a DSC-only evaluation of liquidus viscosity by combining the abovementioned approach for determining viscosity by DSC⁶ with the method for measuring T_L by DSC.¹¹ We have determined the liquidus viscosity of 3 aluminosilicate glasses, one borate glass, and 3 vanadium tellurite glasses using solely DSC. We then compare these results to the η_L values obtained with the standard viscometric method. The liquid compositions cover a wide range of fragilities, and the liquidus viscosity values span over five orders of magnitude.

2. Experimental procedure

The three aluminosilicate glasses are basaltic glass fiber compositions denoted as AS1, AS2, AS3 based on the increasing concentration of alkaline earth oxides (the specific compositions are confidential). The composition of the borate glass is 20Na₂O-10CaO-69B₂O₃-1Fe₂O₃ (mol%). The three vanadium tellurite glasses are called VT10, VT50, VT65, and the compositions are 10V₂O₅-90TeO₂, 50V₂O₅-50TeO₂, and 65V₂O₅-35TeO₂ (mol%), respectively. All glasses were prepared by the

melt-quenching method.^{12,13} Both high and low temperature viscosity measurements were conducted on the bulk glass samples. The high temperature viscosities were determined using a concentric cylinder viscometer. The low temperature viscosities were measured by micro-penetration viscometry. More details of the viscosity measurements can be found elsewhere.^{13,14} $T_{g,vis}$ and m_{vis} were determined by fitting the measured viscosity data to the MYEGA model.

DSC measurements (Netzsch STA 449F3 Jupiter system) were performed to determine calorimetric glass transition temperature and fragility, i.e., $T_{g,DSC}$ and m_{DSC} , respectively. The glass samples were subjected to several DSC scans at different heating rates (q) (between 5 and 30 K/min), where the reheating and the prior cooling rates were always equal. T_f were calculated from the heat flow curves, and the T_f value calculated from the DSC upscan at 10 K/min (equal to the prior downscan rate) is defined as the standard T_g value, i.e., $T_{g,DSC}$.¹⁵ After obtaining the T_f values at various scan rates, the slope of $\log(1/q)$ vs. T_g/T_f was calculated to determine the calorimetric fragility.² This method has been described in detail elsewhere.⁶ Moreover, the DSC scans were carried out to determine T_L at 10, 20, 30 K/min for all the glass samples. The samples were heated up to 50–100 K above T_L . Liquidus temperature, T_L , is determined as the offset temperature of the melting peak, which is the intersection of tangents to the curve, traced on the baseline and on the peak side (Fig. 1). This method is called the “tangent method”, which has uncertainties of approximately ± 2 to 3 K.

3. Results and discussion

Fig. 1 shows the DSC scan curves of VT10 measured at different heating rates. Since vanadium tellurite glasses have strong tendency to crystallize, it exhibits three well-defined characteristic peaks upon heating: an endothermic glass transition peak, an exothermic crystallization peak, and an endothermic melting peak. T_L is determined as the offset temperature of the melting peak using the “tangent method”. It is seen from the curves that the observed T_L increases with increasing heating rate.

In order to obtain the equilibrium T_L , the T_L values determined at different heating rates were fit linearly and extrapolated to 0 K/min. The T_L extrapolations of VT10, together with other glasses, are displayed in Fig. 2. Generally, the slope of the linear fitting lines for glass compositions exhibiting low T_L is lower than that of glass systems with high T_L . In other words, the dynamic effect, i.e., the

scan rate dependence of T_L is more dramatic for high T_L glasses. The error of the equilibrium T_L determination method using DSC is around ± 4 K. The equilibrium T_L values obtained for the seven glasses ranges from 807 K for VT50 to 1489 K for AS3 (listed in Table 1).

The calorimetric glass transition temperature and fragility ($T_{g,DSC}$ and m_{DSC}) of the seven glasses have been determined by DSC measurements. Since there is a deviation between the calorimetric and kinetic fragilities, a correction is needed.⁶ The calorimetric fragility was then converted to kinetic fragility by applying an empirical model described in Ref. ⁶:

$$m_{vis} = 1.289(m_{DSC} - m_0) + m_0 \quad (3)$$

Where $m_0=14.97$. The same correction also applies to dilatometry-derived fragility values.¹⁶ By using the calculated kinetic fragility and $T_{g,DSC}$, together with $\eta_{\infty}(x)=10^{-2.93}$ Pa·s, the viscosity value at any temperature can be calculated using the MYEGA equation.⁶ We have determined T_L values for the seven glass-forming liquids using DSC as mentioned above. By combining the two methods, we calculate η_L solely using DSC, which can be termed the DSC η_L . Meanwhile, we have also obtained the kinetic glass transition temperature and fragility ($T_{g,vis}$ and m_{vis}) by fitting the measured viscosity data to the MYEGA model. By applying $T_{g,vis}$ and m_{vis} , as well as T_L values determined through DSC, the standard η_L has also been calculated. The T_g , m and equilibrium T_L values have been listed in Table 1. The standard η_L and DSC η_L of the seven glasses have been compared in Fig. 3, and excellent agreement is found.

The results in Fig. 3 show that the approach for determining η_L by DSC works well over a very wide range of η_L covering at least 5 orders of magnitude. The studied compositions include widely different oxide glass systems such as aluminosilicates, borates, and vanadium tellurites. Moreover, the method can work both on simple and complex multicomponent glasses, e.g., the aluminosilicate glasses containing more than 8 components. The fragility of the seven glasses ranges from 43 to 108, covering both medium fragility and highly fragile regions. It should be mentioned that this method works not only on glasses that are easy to crystallize, but also on good glass formers which do not show any crystallization or melting peak in DSC scan. For the latter case, the glass

could be heat treated at the crystallization temperature for sufficient time to induce crystallization. Then the melting peak is shown in DSC curve, and T_L can be determined.

In applying the DSC approach for determining η_L , only four small glass disks are needed, where each disk is around 20-50 mg. More importantly, the whole measurement can be done with just a DSC. One sample is used to get the calorimetric glass transition temperature and fragility for viscosity calculations. The remaining three samples are used for the DSC scans to obtain T_L . Since the sample will melt after the scan above T_L , each scan rate will consume one sample. In addition to the small amount of sample needed, the temperature is precisely controlled within the DSC, so the thermal signal is well captured. Since the DSC scans take only a couple of hours, the method is very time efficient. The DSC method is simple to apply, since it avoids the difficulty and complexity of both viscosity and T_L measurements. This method is potentially useful for both fundamental glass science and in the glass industry.

4. Conclusion

We have developed a DSC-only determination of liquidus viscosity by combining the approaches for calculating viscosity and measuring T_L using DSC. The method has been tested on seven glass-forming liquids covering a wide range of fragility values. The liquidus viscosity values of the glass systems determined by DSC have been compared with the standard values, exhibiting good agreement. The method works well over more than five orders of magnitude in liquidus viscosity, and it can be applied to systems with either good or poor glass-forming ability. The DSC method is simpler and more efficient compared to using direct measurements of viscosity and T_L .

Acknowledgement:

Q. Zheng acknowledges support by National Natural Science Foundation of China (51802165), Shandong Provincial Universities Young Innovative Talent Incubation Program, and Shandong Provincial Key Project Funding (2018YFJH0402).

References:

1. Varshneya AK, Mauro JC. Fundamentals of inorganic glasses. 3rd Edition. Amsterdam, Netherlands: Elsevier; 2019.
2. Zheng QJ, Zhang YF, Montazerian M, Gulbitten O, Mauro JC, Zanutto ED, Yue YZ. Understanding glass through differential scanning calorimetry. *Chem Rev.* 2019; 119: 7848-939.
3. Jiusti J, Zanutto ED, Cassar DR, Andreetta MRB. Viscosity and liquidus-based predictor of glass-forming ability of oxide glasses. *J Am Ceram Soc.* 2020;103:921-32.
4. Yue YZ, Zheng QJ. Fiber spinnability of glass melts. *Int J Appl Glass Sci.* 2017;8:37-47.
5. Zheng QJ, Mauro JC. Viscosity of glass-forming systems. *J Am Ceram Soc.* 2017;100:6-25.
6. Zheng QJ, Mauro JC, Yue YZ. Reconciling calorimetric and kinetic fragilities of glass-forming liquids. *J Non Cryst Solids.* 2017;456:95-100.
7. Mauro JC, Yue YZ, Ellison AJ, Gupta PK, Allan DC. Viscosity of glass-forming liquids. *P Natl Acad Sci USA.* 2009;106:19780-4.
8. Zheng QJ, Mauro JC, Ellison AJ, Potuzak M, Yue YZ. Universality of the high-temperature viscosity limit of silicate liquids. *Phys Rev B.* 2011;83:212202.
9. Angell CA. Formation of glasses from liquids and biopolymers. *Science.* 1995;267:1924.
10. Mauro JC, Loucks RJ, Gupta PK. Fictive temperature and the glassy state. *J Am Ceram Soc.* 2009;92:75.
11. Ferreira EB, Lima ML, Zanutto ED. DSC method for determining the liquidus temperature of glass-forming systems. *J Am Ceram Soc.* 2010;93:3757-63.
12. Smedskjaer MM, Mauro JC, Sen S, Yue YZ. Quantitative design of glassy materials using temperature-dependent constraint theory. *Chem Mater.* 2010;22:5358.
13. Kjeldsen J, Rodrigues ACM, Mossin S, Yue YZ. Critical V_2O_5/TeO_2 ratio inducing abrupt property changes in vanadium tellurite glasses. *J Phys Chem B.* 2014;118:14942.
14. Zheng QJ, Mauro JC, Smedskjaer MM, Youngman RE, Potuzak M, Yue YZ. Glass forming ability of soda lime borate liquids. *J Non-Cryst Solids.* 2012;358:658.
15. Yue YZ. Characteristic temperatures of enthalpy relaxation in glass. *J Non-Cryst Solids.* 2008; 354:1112.
16. Ding LF, Qu CH, Yang YJ, Wilkinson CJ, Lee KH, DeCeanne AV, Doss K, Mauro JC. Dilatometric fragility and prediction of the viscosity curve of glass-forming liquids. *J Am Ceram Soc.* 2020, DOI:10.1111/jace.17125.

Figure captions

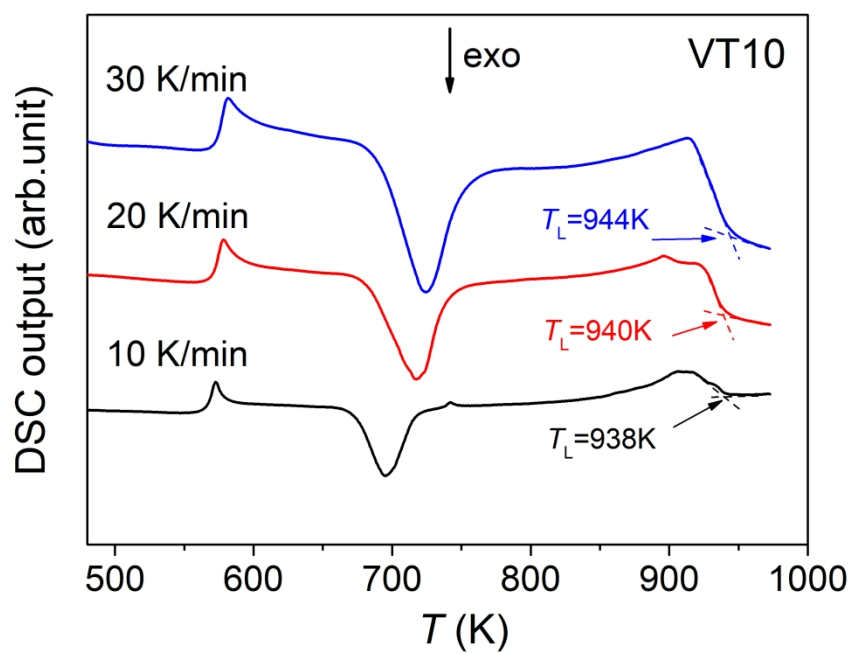
Figure 1. DSC scan curves of VT10 measured at different heating rates (10 K, 20 K, 30 K/min). T_L is determined as the offset temperature of the melting peak.

Figure 2. The dependence of T_L on DSC heating rates (q) for the seven studied glasses. The dashed lines are the linear fitting of the curves. The equilibrium T_L values are determined by extrapolating the linear fitting line to 0 K/min.

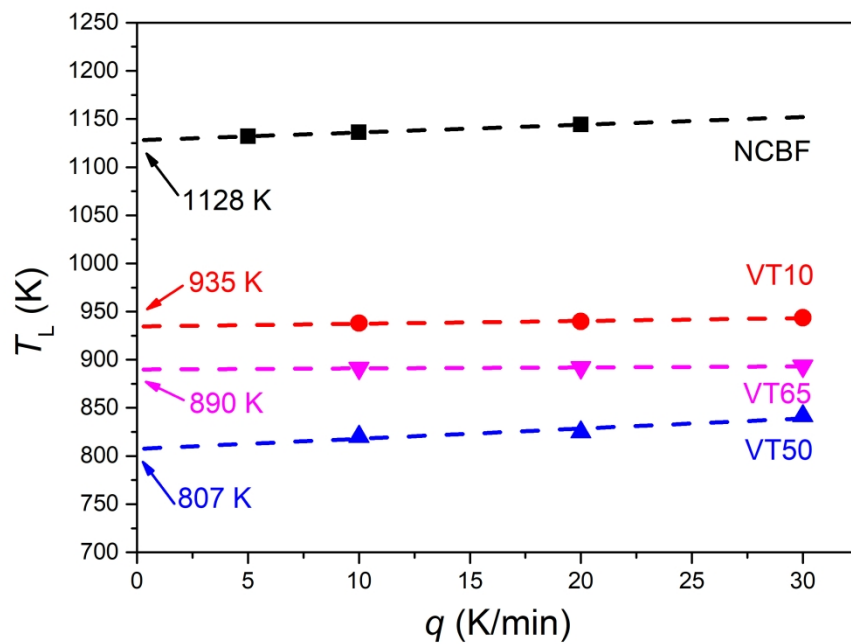
Figure 3. Comparison of $\log \eta_L$ determined by DSC and viscosity measurements. The dashed line is $y = x$ line. The error bars (both the horizontal and vertical directions) are smaller than the symbols.

Table 1 Glass transition temperature determined from viscosity ($T_{g,vis}$) and DSC measurements ($T_{g,DSC}$), liquid fragility index determined from viscosity (m_{vis}) and calculated from DSC measurements (m_{cal}), and the equilibrium T_L values determined from DSC measurements of the seven studied glasses.

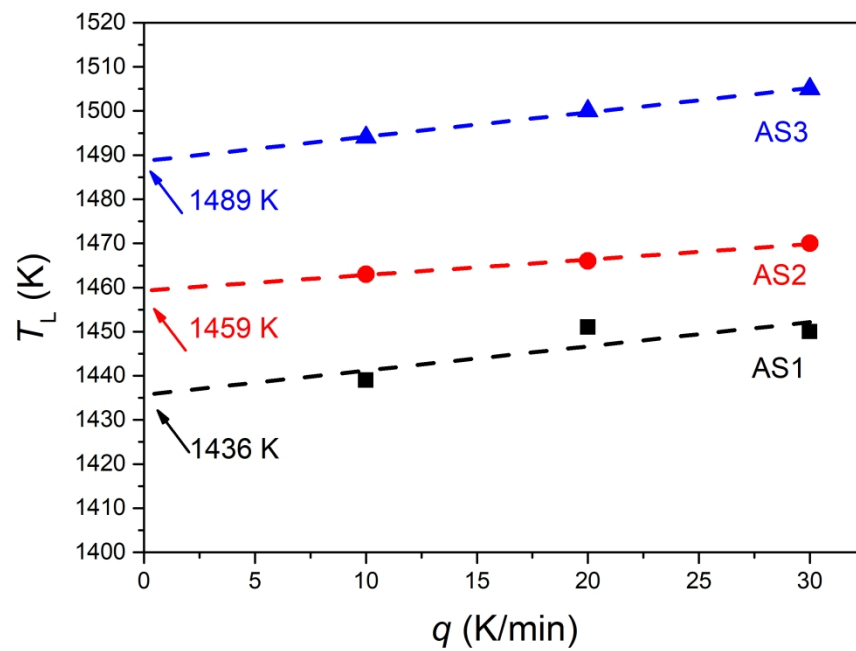
| Glass ID | $T_{g,vis}$ (K) | $T_{g,DSC}$ (K) | m_{vis} (-) | m_{cal} (-) | T_L (K) |
|-----------------|-----------------------------------|-----------------------------------|---------------------------------|---------------------------------|-----------------------------|
| AS1 | 953 | 940 | 45 | 42 | 1436 |
| AS2 | 946 | 937 | 43 | 42 | 1459 |
| AS3 | 947 | 943 | 54 | 50 | 1489 |
| NCB | 765 | 768 | 67 | 70 | 1128 |
| VT10 | 552 | 559 | 84 | 81 | 935 |
| VT50 | 502 | 507 | 88 | 85 | 807 |
| VT65 | 489 | 500 | 108 | 115 | 890 |



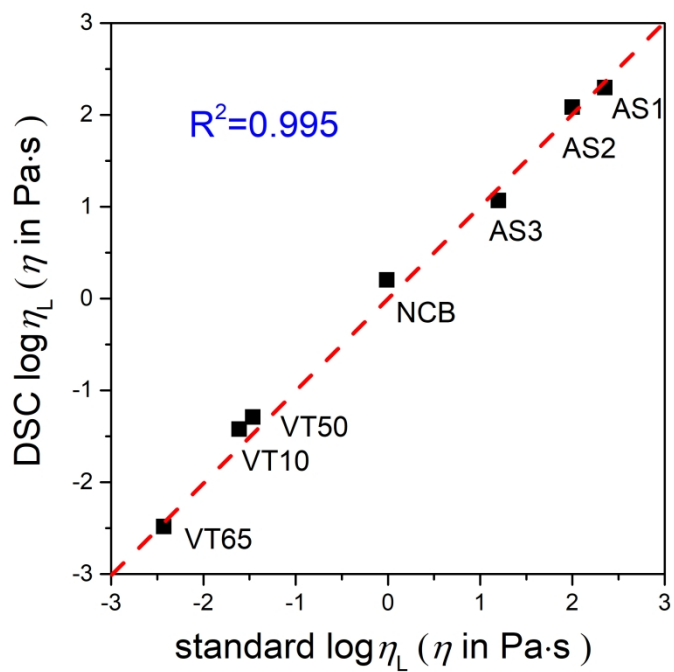
jace_17363_f1.jpg



jace_17363_f2a.jpg



jace_17363_f2b.jpg



jace_17363_f3.jpg