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J. Phys. Chem. B, 2009, 113 (15), 5168-5171• DOI: 10.1021/jp8110327 • Publication Date (Web): 06 March 2009

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Enthalpy Relaxation upon Glass Transition and Kinetic Fragility of Molecular Liquids

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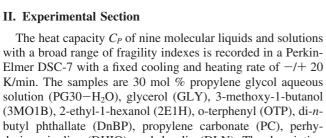
Received: December 15, 2008; Revised Manuscript Received: February 2, 2009

Relaxation enthalpies in the vicinity of glass transitions were recorded on the basis of the heat capacity curves measured in nine glass-forming molecular liquids and solutions in the well defined cooling and subsequent heating cycles. It is observed that enthalpy hysteresis in the cooling/heating cycles is less significant in liquids with increasing fragility. A notable correlation of the fragility index m with relaxation enthalpy ΔH_{R} , glass transition temperature, and heat capacity jump from glasses to liquids is demonstrated. The introduction of $\Delta H_{\rm R}$ favors the thermodynamic evaluation of fragility in the glass forming multicomponent systems such as solutions and alloys.

I. Introduction

Liquid fragility gauges the deviation of the temperature dependence of liquid dynamics from the simple thermally activated (Arrhenius-type) mode in high viscous regime near glass transition. The definition divides liquids into two categories: strong and fragile. A digital description of fragility is basically referred as to the m value, $m = d \log x/d(T_g/T)$ at T_g , where x is viscosity or structural relaxation time, and $T_{\rm g}$ is the glass transition temperature.^{1,2} The interpretation of fragility proves significant in understanding glass transition and liquid physics and has been explored with experimental and theoretical studies.³⁻⁶ Thermodynamically, excess vibrational degrees of freedom (entropy) in liquids relative to crystals were argued to be favored in fragile liquids;^{7,8} and the fragility correlation with the experimentally accessible thermodynamic properties such as $T_{\rm g}$, heat capacity jump ΔC_P at $T_{\rm g}$, and the ratio of liquid C_P over crystal or glass ones, 10 have been tested. However, no reliable relation is otherwise straightforward. Our recent studies quantify the fragility by using the thermodynamic properties: $m = 56T_{\rm g}\Delta C_P(T_{\rm g})/\Delta H_{\rm m}$, where $\Delta H_{\rm m}$ is the heat of fusion, ¹¹ and this correlation was justified with theoretical studies. 12 For most simple one-component systems the equation proves valid, but it is challenged with some exceptions.11 In addition, the application of the equation in complex glass-forming systems such as solutions and alloys is intractable. In this paper, we intend to demonstrate new thermodynamic characters in glass forming liquids of diverse fragility by focusing on the enthalpy relaxation occurred in the quenched glasses upon heating and, in particular, to explore the thermodynamic link to fragility.

droisoquinoline (DHIQ), and decalin (DLN). The description of the chemicals is available elsewhere. 13,14 The majority of



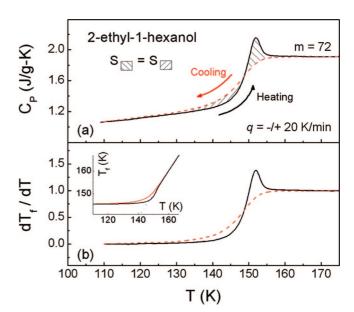


Figure 1. (a) Heat capacity curves of 2E1H during the cooling and heating measurements at the cooling/heating rates of -/+ 20 K/min; (b) fictive temperatures (inset) and the temperature derivatives converted from the heat capacity measurements. The fragility is determined on the basis of the calorimetric method, as outlined in ref 13.

samples follow similar temperature programs: cooling from T_g + 30 K to $T_{\rm g}$ - 50 K and subsequently heating back to the starting points. The samples are held at the two temperatures for 1 min. 3MO1B is an exception due to the limited low temperature range of the instrument. The choices of the upper and lower temperature limits prove to guarantee the molecular liquids and glasses to be "stable" enough at the two temperatures, 15 and the enthalpy relaxation and progressive enthalpy recovery in the glasses upon heating can be, therefore, covered in the temperature ranges. The system is calibrated prior to the measurements. 13,16

III. Results and Discussion

Figure 1a presents the heating and cooling C_P curves of 2-ethyl-1-hexanol. The difference of the two curves was well explained in terms of the enthalpy relaxation and subsequent

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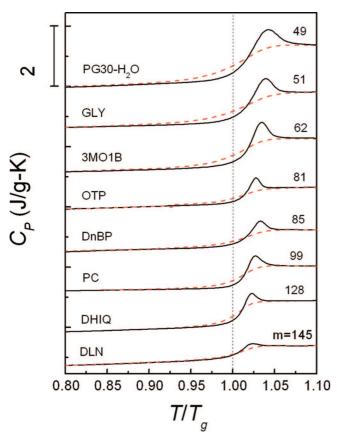


Figure 2. Heat capacity curves measured in the cooling and heating processes in eight organic glass-forming liquids with broad fragility range as a function of reduced temperatures to their glass transitions. All the curves were measured at the cooling/heating rates of -/+ 20 K/min. T_g is the glass transition temperatures, and m is the fragility index. The liquids are 30 mol % propylene glycol aqueous solution (PG30-H₂O), glycerol (GLY), 3-methoxy-1-butanol (3MO1B), 2-ethyl-1-hexanol (2E1H), o-terphenyl (OTP), di-n-butyl phthallate (DnBP), propylene carbonate (PC), perhydroisoquinoline (DHIQ), and decalin (DLN).

enthalpy recovery in the quenched glasses upon heating through the glass transition, ^{17–20} and the two shade regions therefore hold the same areas to guarantee the energy conservation in the cycle of the cooling and heating. Similar construction on the basis of heat capacity or thermal expansion was reported by using dT_f/dT , where T_f is the fictive temperature.²¹ The fictive temperature, which was defined as the temperature at which the properties of a vitreous system in a given state are equal to those of the equilibrium liquid,^{22,23} has been used as a measure of the structural and energy state of a liquid or a glass. ^{24,25} Below $T_{\rm g}$ it keeps constant, whereas above $T_{\rm g}$ it merges into actual temperature ($T_{\rm f} = T$). Fictive temperature can be determined with the C_P measurement of a quenched glass during its reheating by using Moynihan's method.²³ dT_f/dT curves converted from the heating and cooling C_P measurements of 2E1H are presented in Figure 1b. The detailed account of the conversion is available elsewhere. 26,27

Figure 2 shows the heating and cooling C_P curves of more glass-forming liquids with temperature normalized to their $T_{\rm g}$ values. The fragility indexes of the liquids shown here are determined mainly in terms of the calorimetric method, which is based on the $T_{\rm f}$ dependence of the cooling rate Q, $Q = Q_0$ $\exp(-E_a/RT_f)$, where E_a is the apparent glass transition activation energy. Fragility index m is further calculated with the expression, $E_a/(\ln 10RT_g)$. The detailed description was given in refs 13 and 14. 3MO1B is an exception, and the m index was

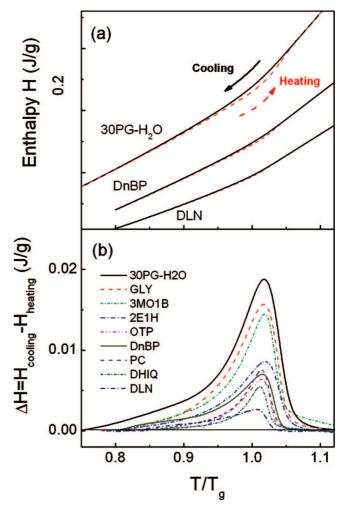


Figure 3. (a) The enthalpy curves upon cooling and subsequent heating in three typical glass-forming liquids with notable fragility difference; (b) Enthalpy difference between the cooling and heating processes. The enthalpy relaxation and enthalpy recovery in the cooled glasses upon heating across glass transition is visible relative to the standard cooling curves.

obtained with the measurements of dielectric relaxation.¹⁴ For most cases, the enthalpy relaxations are argued to be associated with the structural relaxation, (alpha-) relaxation with the activation energies comparable to those derived from viscosity measurements. 11,18,28 Although it is claimed that the decoupling between enthalpy relaxation and viscous flow might exist in some fragile liquids,²⁹ our studies of molecular liquids do not show notable decoupling, even in the case of the most fragile molecular liquid, decalin ($m \approx 145$). ^{13,30}

The less difference of the C_P curves measured from the heating and cooling programs was observed with increasing fragility. The enthalpies of liquids and glasses is calculated with the integral of the C_P curves, as shown in Figure 3a. Three liquids with significant fragility discrepancy are selected to be presented. The heating and cooling enthalpy curves differ remarkably for PG-H₂O with a visible thermal hysteresis, whereas the difference is trivial for decalin.

The difference was magnified in Figure 3b, covering all the studied liquids with an emphasis of the enthalpy relaxation and subsequent recovery. The maximal value in Figure 3b represents the relaxation depth. When we use ΔH_R to define the total relaxation enthalpy during the heating, $\Delta H_{\rm R}$ is therefore equal to the area of each of the shade regions in Figure 1, and the peak value in Figure 3b reads $\Delta H_R/T_g$, reduced relaxation heat.

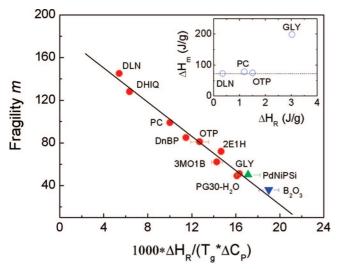


Figure 4. The correlation between fragility and relaxation heat involved in the cooling/heating cycles $\Delta H_{\rm R}$, glass transition temperatures $T_{\rm g}$, and heat capacity jump from glasses to liquids ΔC_P . $\Delta H_{\rm R}$ is determined either with the integral of the shaded region in Figure 1 or from the peak value in Figure 2b multiplied by $T_{\rm g}$. A metallic glass ${\rm Pd}_{40}{\rm Ni}_{40}{\rm P}_{19}{\rm Si}_1$ is also shown, and the data are from ref 34. The data of ${\rm B}_2{\rm O}_3$ is based on the derivative of the fictive temperature converted from the heat capacity measurements (ref 40). The line is a guide for eyes.

Seemingly, a correlation of the relaxation heat with fragility is immediately accessible, but the plot of $\Delta H_{\rm R}$ or $\Delta H_{\rm R}/T_{\rm g}$ as a function of m are less desirable, whereas the attempt of $\Delta H_{\rm R}/T_{\rm g}\Delta C_P$ proves a better formalism otherwise, and the result is shown in Figure 4. The correlation of $\Delta H_{\rm R}/T_{\rm g}\Delta C_P$ with fragility is obvious, reminiscent of the recent result, $m=56T_{\rm g}\Delta C_P(T_{\rm g})/\Delta H_{\rm m}$.

It needs to be noted that either $\Delta H_R/T_g\Delta C_P$ or $T_g\Delta C_P/\Delta H_R$ would generate acceptable correlation with fragility; however, the analysis and comparison of correlation coefficients in the two cases favors the former one. Experimental data seem not to imply a relation of $\Delta H_{\rm R}$ to $\Delta H_{\rm m}$ is not straightforward, as shown in the insert of Figure 4; therefore, the substitution of ΔH_R for $\Delta H_{\rm m}$ in terms of $m \approx T_{\rm g} \Delta C_P(T_{\rm g}) / \Delta H_{\rm m}$ is not expected to improve the degree of the correlation. It is seen that $\Delta H_{\rm m}$ of the studied systems does not reach zero with the approach of $\Delta H_{\rm R}$ to zero, but nearly stays on a constant of ~68 J/g.³¹ The comparison of $\Delta H_{\rm R}$ with $\Delta H_{\rm m}$ suggests that the former is just a fraction of the latter.³² For example, $\Delta H_R/\Delta H_m$ of glycerol is \sim 1%, and for the other less strong molecular liquids the ratios are even lower. Apparently, ΔH_R is more glass-transition-related, and it might be expected to work better than $\Delta H_{\rm m}$. This is the case of decalin. The calculation of fragility of decalin with the use of $\Delta H_{\rm m}$ gave a remarkable deviation from the experimental determination, ¹¹ whereas the substitute of $\Delta H_{\rm m}$ by $\Delta H_{\rm R}$ appears to correct the deviation, as seen in Figure 4. The use of relaxation enthalpy involved in the well defined cooling/heating processes around glass transitions therefore assists to evaluate the liquid fragility. Recent studies of the enthalpy relaxation in the hyperquenched inorganic oxide glasses with the thermodynamic and dynamic parameters of interest were reported and,³³ notwithstanding some difference in the cooling rates, a test of the correlation of $\Delta H_R/T_g\Delta C_P$ with fragility can be therefore expected among the oxide glasses. On the basis of the data (Table 2 in ref 33), the correlation turns out to be positive.

Besides the molecular liquids, Figure 4 concerns a binary solution, $PG30-H_2O$, and a metallic glass-forming alloy, $Pd_{40}Ni_{40}P_{19}Si_1$. The thermodynamic data of the alloy were taken from ref 34, and the fragility index referred to the data of

Pd₄₀Ni₄₀P₂₀ reported in refs 21 and 35. The results of both the solution and the alloy prove to be subject to the master curve generated from the molecular liquids. The present studies therefore emphasize the advantage of the application of $\Delta H_{\rm R}$ instead of to $\Delta H_{\rm m}$ to evaluate the liquid dynamics. Some studies suggested that the multicomponent systems usually exhibit a marked mismatch of the ideal thermodynamic and dynamic glass transition, $T_{\rm K}$ and T_0 (the former is defined as a temperature where the excess entropy of liquids relative to that of crystals approaches to zero, and the latter is a temperature where viscosity or relaxation time diverges in terms of the empirical Vogel-Fulcher-Tammann equation). 36,37 The difference largely exceeds what is expected from the fragility-dependent mismatch.³⁸ Thus, the use of $T_g\Delta C_P(T_g)/\Delta H_m$ to the multicomponent systems might not lead to reliable fragility indexes, whereas the introduction of $\Delta H_{\rm R}$ in the present work turns out to succeed in obtaining the reliable fragility indexes in alloys and solutions.

Figure 4 also highlights the case of B₂O₃, for which the glass transition thermodynamics and dynamics have been well studied. 11,39 The temperature derivatives of the fictive temperatures T_f , which are converted from C_P curves during a well defined cooling/heating cycle around glass transition, have been documented. 23,40 In analogy to $\Delta H_{\rm R}$, the integral of the heating and cooling dT_f/dT generates ΔT_f , the maximal T_f difference in the heating curve relative to the cooling one. For this case, the abscissa in Figure 4 appears to be $\Delta T_{\rm f}/T_{\rm g}$. Previous studies have exhibited a formulism to calculate fictive temperatures through relaxation enthalpy, and it is not unexcepted that $\Delta H_R/\Delta C_P$ is equivalent to $\Delta T_{\rm f}^{-13,33,41}$ The data analyses of the heating and cooling C_P curves in Figure 1a and Figure 2 in terms of $T_{\rm f}$ concept, as presented in the inset of Figure 1b, confirm the consistency of the two expressions. Therefore, the data of B₂O₃ can be reasonably incorporated in Figure 4 and indicate an excellent agreement with the master line generated on the basis of the molecular liquids.

Finally, it needs to be addressed that dT_f/dT of B_2O_3 was also reported on the basis of the volume relaxation with the measurements of the cooling/heating expansion coefficient α , and this allows the direct comparison between the α -based T_f results. The data analyses suggested that the maximal ΔT_f involved in the enthalpy relaxation and the volume relaxation with the comparable cooling/heating temperature programs matches well. It seems that the present study in correlating enthalpy relaxation with fragility can be extended to volume relaxations, and $\Delta V_R/\Delta \alpha V T_g$ (ΔV_R is relaxation volume, $\Delta \alpha$ is the difference of the coefficients of volumetric thermal expansion of liquids and glasses at T_g , and V is the volume of glasses) is expected to scale with fragility, in parallel with $\Delta H_R/\Delta C_P T_g$.

IV. Conclusion

The enthalpy relaxation involved in a well defined cooling and heating cycle around the glass transition shows a notable correlation with the kinetic fragility. The introduction of relaxation enthalpy $\Delta H_{\rm R}$ instead of heat of fusion $\Delta H_{\rm m}$ favors the evaluation of liquid fragility of multicomponent glassforming systems such as alloys and solutions. A new thermodynamic correlation of liquid fragility by covering more glass forming systems is therefore presented. The present studies can be extended to volume relaxation to evaluate liquid fragility.

Acknowledgment. The data were acquired at Arizona State University under NSF-DMR support and are used in this work with the encouragement of Professor C. A. Angell. This work was supported by the National Science Foundation of China

(Grant No. 10804093), and the Scientific Research Foundation for the Returned Scholars Hebei Province.

References and Notes

- (1) Angell, C. A. In *Relaxations in Complex Systems*, Ngai, K. L.; Wright, G. B. Eds.; National Technical Information Service, U.S. Department of Commerce: Springfield, VA, 1985.
- (2) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. J. Appl. Phys. **2000**, 88, 3113.
 - (3) Rössler, E.; Sokolov, A. P. Chem. Geo. 1996, 128, 143.
- (4) Ngai, K. L. J. Non-Cryst. Solids 2000, 275, 7. Ngai, K. L.; Bao, L.-R.; Yee, A. F.; Soles, C. L. Phys. Rev. Lett. 2001, 87, 215901.
- (5) Novikov, V. N.; Sokolov, A. P. *Nature(London)* **2004**, *431*, 961. Novikov, V. N.; Sokolov, A. P. *Philos. Mag.* **2006**, *86*, 1567.
 - (6) Sastry, S. Nature(London) 2001, 409, 164.
- (7) Martinez, L.-M.; Angell, C. A. Nature(London) 2001, 410, 663. Angell, C. A. J. Phys.: Condens. Matter 2000, 12, 6463.
 - (8) Wang, L.-M.; Richert, R. Phys. Rev. Lett. 2007, 99, 185701.
- (9) Angell, C. A. Science 1995, 267, 1924. Angell, C. A. J. Res. Natl. Inst. Stand. Technol. 1997, 102, 171.
 - (10) Huang, D.; McKenna, G. B. J. Chem. Phys. 2001, 114, 5621.
- (11) Wang, L.-M.; Angell, C. A.; Richert, R. J. Chem. Phys. **2006**, 125, 074505. Wang, L.-M.; Angell, C. A. J. Chem. Phys. **2003**, 118, 10353.
- (12) Stevenson, J. D.; Wolynes, P. G. J. Phys. Chem. B 2005, 109, 15093.
- (13) Wang, L.-M.; Velikov, V.; Angell, C. A. J. Chem. Phys. 2002, 117, 10184.
- (14) Wang, L.-M.; Richert, R. J. Chem. Phys. 2004, 121, 11170. Wang, L.-M.; Richert, R. J. Phys. Chem. B 2007, 111, 201.
- (15) The quenched glasses keep on nonequilibrium states and might relax towards metastable states by releasing heat. At temperature as low as 50 K below T_g , as we used in the work, the relaxation dynamics is extremely slow, and the short-time aging (for example, 1 min) does not produce a visible effect.
- (16) Velikov, V.; Borick, S.; Angell, C. A. J. Phys. Chem. B 2002, 106, 1069.
- (17) Davies, R. O.; Jones, G. O. Proc. Roy. Soc. Ser. A 1953, 217, 26.
- (18) Moynihan, C. T.; Easteal, A. J.; Wilder, J.; Tucker, J. J. Phys. Chem. **1974**, 78, 2673.
- (19) Mitsch, C.; Görler, G. P.; Wilde, G.; Willnecker, R. J. Non-Cryst. Solids **2000**, 270, 172.

- (20) Chen, H. S.; Katoa, H.; Inoue, A.; Saida, J.; Nishiyama, N. *Appl. Phys. Lett.* **2001**, *79*, 60. Chen, H. S.; Katoa, H.; Inoue, A.; Saida, J.; Nishiyama, N. *J. Non-Cryst. Solids* **1981**, *46*, 289.
 - (21) Brüning, R.; Sutton, M. J. Non-Cryst. Solids 1996, 205, 480.
- (22) Tool, A. Q. J. Chem. Soc. Ceram. 1946, 29, 240. Narayanaswamy, O. S. J. Chem. Soc. Ceram. 1971, 54, 491.
- (23) Moynihan, C. T.; Easteal, A. J.; Debolt, M. A.; Tucker, J. J. Am. Ceram. Soc. 1976, 59, 12.
 - (24) Angell, C. A.; Wang, L.-M. Biophys. Chem. 2003, 105, 621.
- (25) Swallen, S. F.; Kearns, K. L.; Mapes, M. K.; Kim, Y. S.; McMahon, R. J.; Ediger, M. D.; Wu, T.; Yu, L.; Satija, S. *Science* **2007**, *315*, 353.
- (26) Hodge, I. M. J. Res. Natl. Inst. Stand. Technol. 1997, 102, 195. Hodge, I. M. J. Am. Ceram. Soc. 2008, 91, 766.
- (27) Wang, L.-M.; Tian, Y. J.; Liu, R. P.; Richert, R. J. Chem. Phys. 2008, 128, 084503.
- (28) Yamamuro, O.; Oishi, Y.; Nishizawa, M.; Matsuo, T. *J. Non-Cryst. Solids* **1998**, 235–237, 517.
- (29) Komatsu, T.; Aida, K.; Honma, T.; Benino, Y.; Sato, R. J. Am. Ceram. Soc. 2002, 85, 193.
 - (30) Duvvuri, K.; Richert, R. J. Chem. Phys. 2002, 117, 4414.
- (31) The analyses of the available data compiled in the *CRC Handbook* of *Chemistry and Physics* (88th Edition, CRC press, 2007) show that without phase transitions in crystals, the heat of fusion of chemicals composed of C and H and C, H, and O is generally no less than 60 J/g. In the cases with phase transitions in crystals, the cumulative heat give the same conclusion.
- (32) Kearns, K. L.; Swallen, S. F.; Ediger, M. D.; Wu, T.; Sun, Y.; Yu, L. J. Phys. Chem. B **2008**, 112, 4934.
 - (33) Hornbøll, L.; Yue, Y. J. Non-Cryst. Solids 2008, 354, 1862.
 - (34) Bruning, R.; Samwer, K. Phys. Rev. B 1992, 46, 11318.
 - (35) Kawamura, Y.; Inoue, A. Appl. Phys. Lett. 2000, 77, 1114
 - (36) Legg, B. A.; Schroers, J.; Busch, R. Acta Mater. 2007, 55, 1109.
 - (37) Fecht, H.-J.; Johnson, W. L. Mater. Sci. Eng., A 2004, 375–377, 2.
 - (38) Tanaka, H. Phys. Rev. Lett. 2003, 90, 055701.
- (39) Böhmer, R.; Ngai, K. L.; Angell, C. A.; Plazek, D. J. J. Chem. Phys. 1993, 99, 4303.
- (40) Debolt, M. A.; Easteal, A. J.; Macedo, P. B.; Moynihan, C. T. J. Am. Ceram. Soc. 1976, 59, 16.
- (41) Wungtanagorna, R.; Schmidt, S. J. Thermochim. Acta 2001, 369, 95

JP8110327