International Journal of Optoelectronic Engineering 2012, 2(5): 26-29
DOI: 10.5923/j.ijoe.20120205.01

The Correlation between Reduced Glass Transition Temperature and Glass Forming Ability of Undercooled Polymeric Glasses

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Abstract The thermodynamic behaviour of glass forming undercooled melt have been studied by analysing the temperature dependence of the Gibbs free energy difference (*ΔG*) for six polymeric glass forming materials[O-terphenyl, Tri-α-naphthylbenzene, Glycerol, Ethanol, 2-methylpentane and Phenylsalicylate (salol)] between the undercooled melt and the corresponding equilibrium solid phases. The expression obtained by expanding free energies of the undercooled liquid and solid phases of the materials in the form of Taylor's series expansion. The procedure for the estimation of the ideal glass transition temperature has been reviewed together its importance in the glass forming ability of materials. The glass forming ability of undercooled materials is also explained in terms of ratio of reduced glass transition temperature and ideal glass transition temperature. It has also reported that Glycerol has the largest melting interval with the poorest glass forming ability among these six polymers. It has also been found that the best polymeric glass forming materials are at near eutectic composition. There is a strong correlation between glass forming ability of these polymeric materials.

Keywords Glass Transition Temperature, Undercooled, Taylor's Series Expansion, Ideal Glass Transition Temperature

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1. Introduction

The thermodynamic behaviour of glass forming polymeric melts has been studied employing the expressions based on Taylor's series expansion and it is found that the expression for *ΔG*, obtained are capable to explain temperature dependence of the thermodynamic quantities (*ΔG, ΔH* and *ΔS*) of glass forming polymeric melts quite satisfactorily. It is quite interesting to see the response of expression obtained on the basis of Taylor's series expansion in explaining the temperature dependence of the thermodynamic quantity *ΔG* for glass forming organic liquids.

The present study is for the Gibbs free energy difference (*ΔG)* between liquid and solid phases for glass forming organic melts by calculating *ΔG* for six different samples of organic glasses; o-terphenyl (o-ter), tri-α-napthyle benzene (tri-α-NB), phenyl salicylate (salol), glycerol, ethanol and 2-methylpentane (2-mp) in the temperature range T_m to T_g in the frame of expression based on Taylor's series expansion.

The expression for the entropy difference *ΔS* based on Taylor's series expansion has been further employed to find the Kauzmann temperature (T_K) and the residual entropy (ΔS_R) for all six samples of glass forming organic liquids as stated above. Attempt has been made to correlate T_K and T_g on the basis of results obtained and a linear relation is obtained between (T_g/T_m) and (T_K/T_m). The variation of T_K with $\Delta C_p^m / \Delta S_m$ has also been studied by expressing $T_K/T_m (= \delta)$ in the term of $\Delta C_p^m/\Delta S_m$.

2. Results and Discussion

2.1. Temparature Variation of Δ G

The material constants used in the present analysis are taken from the reports of earlier authors[6-12] and are listed in Table 1. The temperature dependence of the thermodynamic parameter *ΔG* for glass forming organic liquids are studied by estimating *ΔG, ΔH* and *ΔS* of six different samples o-ter, tri-α-NB, salol, glycerol, ethanol and 2-mp in the temperature range T_m to T_g with the help of expressions for the respective parameters based on the Taylor's series expansion

$$\Delta G = \Delta S_m \Delta T - \frac{\Delta C_p^m \Delta T^2}{(T_m + T)} \tag{1}$$

$$\Delta H = \Delta H_m - \Delta C_p^m \Delta T + \left[\frac{\partial C_p}{\partial T}\right]_{Tm} \frac{\Delta T^2}{2!} - \text{.........} \tag{2}$$

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and

$$\Delta S = \Delta S_m - \frac{2\Delta C_p^m \Delta T}{\left(T_m + T\right)} + \left[\frac{\partial \Delta C_p}{\partial T}\right]_{T_m} \frac{\Delta T^2}{\left(T_m + T\right)} \quad (3)$$

and the results obtained are illustrated in Fig. 1 for ΔG along with experimental values. The experimental values of the various thermodynamic quantities ΔG, ΔH and ΔS are calculated with the aid of the basic thermodynamic relations as given

$$\Delta G = \Delta H - T\,\Delta S \quad (4)$$

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT \quad (5)$$

$$\Delta S = \Delta S_m - \int_T^{T_m} \frac{\Delta C_p}{T} dT \quad (6)$$

and experimental data of ΔC_p in the form of

$$\Delta C_p = a + b\,T \quad (7)$$

which is found to be correct for the most of organic simple liquids. Where a and b are constants.

The variation of ΔG for the glass forming organic liquids can be studied with the help of Fig. 1 which shows a very good agreement between calculated and experimental values of ΔG in the entire temperature range T_m to T_g for all samples. It is interesting to note that nature of variation of the thermodynamic quantity ΔG with temperature is almost similar for all samples. In view of results illustrated in Fig. 1, it can be said that the response of the expression for ΔG obtained in the frame of Taylor's series expansion is very good for explaining the temperature dependence of thermodynamic quantity ΔG of glass forming organic liquids also. At the same time, these expressions are quite simple and require the knowledge of ΔC_p^m, ΔS_m and T_m which can be measured experimentally without having much complications.

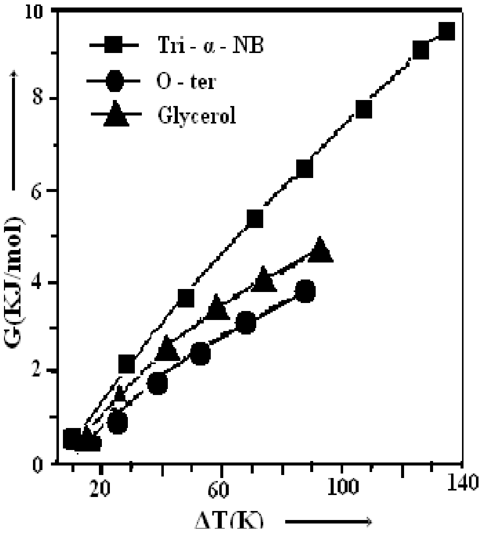

Figure 1. Gibbs free energy (ΔG) and Temperature difference (ΔT) for the three organic compounds have been shown. The symbols explain the experimental and Line denoted the calculated values respectively

An attempt is made in Table 2 to compare the values of ΔG estimated on the basis of earlier expressions reported by Turnbull, Hoffman and Thompson and Spaepen [1-3] and expression used in the present work based on Taylor's series expansion. Glycerol is taken as an example and analysis is made in the temperature range T_m *to* T_g . Table 2 shows that the agreement between the calculated and the experimental values of ΔG for glycerol is best at all temperatures with a discrepancy of about 3.3% at $T = T_g$ for the maximum undercooling of 107 K which can be compared with the discrepancies of about 43.1% , 9.1% and 11.2% at $T = T_g$ obtained in the frame of expressions proposed by Turnbull, Hoffman and Thompson and Spaepen respectively.

Table 1. The material parameters used in the study of the various thermodynamic parameters ΔG, ΔH and ΔS of glass forming organic melts

Materials	a (J/mol/K)	b (J/mol/K^2)	ΔH_m (J/mol)	ΔS_m (J /mol/K)	$\Delta C_p{}^m$ (J /mol/K)	T_m (K)	T_g (K)
O-terphenyle	241.1280	–0.4933	18371	56.01	79.32	328	243.15
Tri-α-NB	311.4245	–0.4673	42489	90.02	90.86	472	342
Salol	307.4800	–0.8964	9799	30.95	23.68	316.6	230
Glycerol	90.8646	–0.0391	18371	62.70	79.42	293	186
Ethanol	51.5810	–0.1673	5015	31.64	25.06	158.5	91
2.Methylpentane	146.8710	–0.7985	6260	52.36	51.41	119.55	79.5

Table 2. Free energy difference ΔG between undercooled liquid and corresponding equilibrium solid phases of glycerol calculated using various expressions of ΔG proposed by earlier investigators. Experimental values of ΔG is evaluated using experimental data of ΔC_p

T (K)	ΔT (K)	ΔG (J / mol / K) of Glycerol				
		Turnbull (1950)	Hoffman (1958)	Thompson and Spaepen (1979)	Present equation (1)	Experimental
290	03	188	187	187	187	186
270	23	1442	1329	1383	1367	1366
250	43	2696	2300	2483	2426	2419
230	63	3590	3100	3474	3359	3321
210	83	5204	3729	4345	4158	4036
186 (T_g)	107	6708	4259	5210	4811	4687

Table 3. The value T_K and ΔS_R for glass forming organic materialsobtained in the present study. T_K^{exp} and ΔS_R^{exp} are based on the experimental data of ΔC_p

Materials	T_K^{cal} (K)	T_K^{exp} (K)	ΔS_R^{cal} (J mol^{-1} K^{-1})	ΔS_R^{exp} (J mol^{-1} K^{-1})	T_K^{exp}/T_m	T_g/T_m	$\frac{(T_g-T_K^{exp})}{T_m}$	$\Delta S_R^{exp}/\Delta S_m$	$\Delta C_p^m/\Delta S_m$
O-ter	196.6	200.2	28.28	25.69	0.6104	0.7413	0.1309	0.4586	1.42
Tri-α-NB	246.6	255.4	57.27	50.44	0.5411	0.7246	0..1835	0.5551	1.01
Salol	202.2	209.5	14.69	10.32	0.6617	0.7265	0.0648	0.3334	0.77
Glycerol	132.0	135.0	29.05	25.69	0.4608	0.6348	0.1740	0.4082	1.27
Ethanol	57.3	58.0	18.22	14.31	0.3660	0.5741	0.2081	0.4523	0.79
2-Methyl pentane	58.9	61.0	27.60	24.42	0.5103	0.6649	0.1546	0.4664	0.98

2.2. Ideal Glass Transition Temperature (T_K)

According to Kauzmann[4], a liquid losses its entropy at a faster rate than the equilibrium solid resulting in the two phases having the same entropy at some temperature T_K which is known as iso-entropic temperature and T_K is below T_g and much above the absolute zero.

The ideal glass transition temperature or iso-entropic temperature plays an important role in the study of viscosity as well as glass formation ability of materials. Thus, it is quite desirable to study T_K . The ideal glass transition temperature T_K can be caculated as

$$\frac{b}{2}(1-\delta)^2+(b-a)\delta-\left(\Delta C_p^m-a+b\right)ln\delta+\Delta S_m=0 \quad (8)$$

where b = $T_m^2\left[\frac{\partial^2\Delta C_p}{\partial T^2}\right]_{T_m}$ and a = $T_m\left[\frac{\partial\Delta C_p}{\partial T}\right]_{T_m}$

The equation stated above is transcendental in nature and can be solved for δ using iterative procedures.

The ideal glass transition temperature T_K has been estimated for six sample of organic material by solving equation (8) using iterative procedure and the values obtained are listed in Table 3. The experimental values of T_K has also been extrapolated using experimental values of ΔC_p and basic thermodynamic relation stated in equation (6) and results obtained are also reported in Table 3 which shows a very good agreement between calculated and extrapolated values of T_K for all samples.

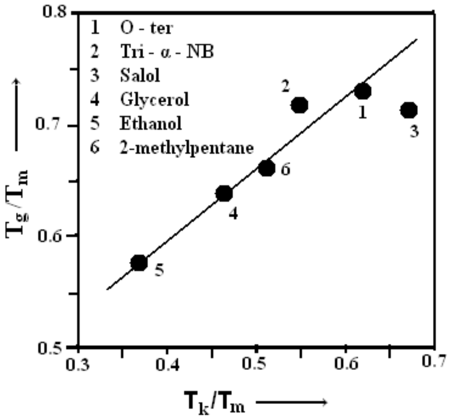

Figure 2. The calculated and experimental values (T_K/T_m) and (T_g/T_m) of all the six samples have been shown

It is interesting to study the variation of the glass transition temperature T_g with the ideal glass transition temperature T_K . The variation of T_g/T_m with T_K/T_m is demonstrated in Fig. 2 for organic materials on the basis of results obtained in the present analysis which shows a linear relation

$$T_g/T_m = 0.7256\ (T_K/T_m) + 0.3068 \quad (9)$$

with correlation coefficient r = 0.9755. A similar relation has also been reported by Mishra and Dubey[16] for the metallic glasses. The average value of T_g/T_K is found to be 1.32 ± 10 % which can be compared with the values 1.30 ± 8.4 % and 1.29 ± 10 % reported by Adam and Gibbs and Bestul and Chang[17-18] respectively. It can also be compared with the value 1.31 ± 14 % and 1.36 ± 21 % reported by Dubey and his co-workers (Dubey et al., Mishra and Dubey[6-7 and 14] based on the relaxation phenomenon.

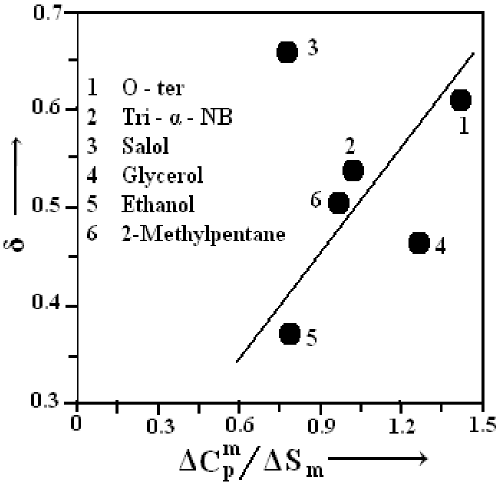

Figure 3. The calculated and experimental values ($\Delta C_p^m/\Delta S_m$) and (δ) of all the six samples have been shown

The ideal glass transition temperature T_K is mainly controlled by the ratio $\Delta C_p^m/\Delta S_m$ and it is interesting to study the variation of T_K with $\Delta C_p^m/\Delta S_m$ which has been illustrated in Fig. 3. An attempt is made to express δ in terms of $\Delta C_p^m/\Delta S_m$ and one can have an empirical relation

$$\delta = 0.4878\ (\Delta C_p^m/\Delta S_m)^{0.8180} \quad (10)$$

with correlation coefficient r = 0.9059. With the help of Fig. 3, it can be seen that the reduced ideal glass transition temperature (T_K/T_m) increases with increasing $\Delta C_p^m/\Delta S_m$ which is similar to the earlier findings of Dubey and Ramachandrarao[6] based on the analysis of different kinds of glasses using the hole theory of liquid.

3. Conclusions

The temperature dependence of the thermodynamic quantities, the Gibbs free energy difference (ΔG), enthalpy difference (ΔH) and entropy difference (ΔS) between the undercooled melt and the equilibrium solid phases has been studied in the framework of Taylor's series expansion for six different samples of glass forming organic liquids in the temperature range T_m to T_g and it is found that the expression stated in equation (1) for ΔG based on Taylor's series expansion is capable of explaining the temperature dependence of respective parameters quite satisfactorily. The value of ΔG obtained in the present work is better than ΔG obtained in the frame of expression reported by earliar worker. At the same time, these expressions require the knowledge of ΔC_p^m, ΔS_m and T_m which can be measured experimentally without much complications.

The ideal glass transition temperature T_K has also evaluated for organic samples on the basis of $\Delta C_p^m / \Delta S_m$ and and $(T_g - T_K)/T_m$. It is found that the ideal glass transition temperature (T_K) is mainly controlled by the ratio $\Delta C_p^m / \Delta S_m$ and there exists a linear relation between T_K/T_m and T_g/T_m. The material having a large $\Delta C_p^m / \Delta S_m$ and large T_K/T_m and such material can be a better glass former as compared to those having a low value of $\Delta C_p^m / \Delta S_m$ and low T_K/T_m.

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