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Measurement of the Glass-Transition Temperature of Simple Liquids

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The glass-transition temperatures of 34 liquids have been measured by differential thermal analysis, and the results compared with the values predicted from viscosity measurements by the equation $\ln\eta = A'' + B''/(T - T_0)$. In those liquids which have two non-Arrhenius viscosity regions, there is good agreement between observed T_g values and those predicted from the lower-temperature form of this equation. In those liquids which have only one observable non-Arrhenius region, measured T_g values are usually lower than those predicted from viscosity measurements. It is suggested that this is caused by a change in non-Arrhenius viscosity behavior at higher viscosities which are unattainable experimentally.

I. INTRODUCTION

MANY liquids, upon sufficient supercooling below their freezing points, exhibit a glass-transition temperature T_g at which certain properties of the liquid such as the coefficient of thermal expansion and the heat capacity change from their liquid-state values to values similar to those of a crystalline solid.[1] It is now established[2] that the glass-transition temperature as conventionally measured is purely a relaxation phenomenon arising from the finite duration of an experiment. In an experiment of infinite duration, a lower limiting value of glass-transition temperature would be observed. This temperature T_0 is a second-order-transition temperature, and is the fundamental reference temperature for all molecular transport and relaxation processes in the liquid.

Values of T_0 may be calculated from studies of the temperature dependence of the viscosity of liquids in the non-Arrhenius region using the equation

$$\ln\eta = A'' + B''/(T - T_0). \tag{1}$$

Here η is the viscosity of the liquid in poise at temperature T, and A'' and B'' are constants. The glass-transition temperature can be calculated from this equation as that temperature at which the viscosity of the liquid is 10^{13} P.[3]

In certain liquids the T_0 equation (1) gives an excellent description of the viscosity over the whole non-Arrhenius temperature range, including the supercooled region, for which experimental data are available. In other liquids, however, it is necessary to apply the equation in two separate temperature regions with two different sets of values of the constants A'', B'', and T_0.[2] It is probable that the changes from Arrhenius to non-Arrhenius behavior and from one type of non-Arrhenius behavior to another are caused by the restriction of the rotation of the molecules in the liquid.[4] In the Arrhenius region, molecules are free to rotate many times about at least two axes during the time between translational jumps. In the higher-temperature non-Arrhenius region, molecules are able to rotate about only one axis during this time, while in the lower-temperature non-Arrhenius region rotation occurs primarily as a result of molecular translational motion.

The object of this paper is to compare the values of the glass-transition temperature predicted by Eq. (1) with those measured experimentally.

II. EXPERIMENTAL

The glass-transition temperatures of the liquids discussed here have been measured by differential thermal analysis (DTA) using a du Pont 900 differential thermal analyzer. One-tenth-milliliter samples of the

[1] W. Kauzmann, Chem. Rev. **48**, 219 (1948).

[2] A. J. Barlow, J. Lamb, and A. J. Matheson, Proc. Roy. Soc. (London) **A292**, 322 (1966).

[3] G. Tammann and W. Hesse, Z. Anorg. Allgem. Chem. **156**, 245 (1926).

[4] D. B. Davies and A. J. Matheson, J. Chem. Phys. **45**, 1000 (1966).

TABLE I. Parameters of the equation $\ln\eta = A'' + B''/(T-T_0)$.

Liquid	A''	B''(°K)	T_0(°K)	RMSE[a]	Range (°K)
"High"-temperature region					
Pent-1-ene	−6.824	245.1	74.2	0.018	113–165
cis-Pent-2-ene	−6.595	221.5	74.0	0.007	116–153
trans-Pent-2-ene	−7.037	266.1	72.5	0.007	130–181
Hex-1-ene	−6.926	275.8	85.1	0.005	126–195
trans-hex-2-ene	−6.838	271.4	88.6	0.004	137–190
Hept-1-ene	−6.832	294.8	95.0	0.013	142–192
cis-Hept-2-ene	−6.725	285.7	92.7	0.013	141–183
cis-Oct-2-ene	−6.723	310.1	104.1	0.005	153–211
Methyl cyclohexane	−7.688	626.1	73.5	0.010	138–208
Ethyl cyclohexane	−7.008	466.7	94.3	0.014	152–238
Isopropyl cyclohexane	−6.728	421.3	112.6	0.011	168–243
n-Butyl cyclohexane	−7.194	493.5	120.4	0.007	183–302
sec-Butyl cyclohexane	−6.777	411.3	127.1	0.009	180–273
n-Pentyl cyclohexane	−7.044	483.6	130.2	0.011	195–304
n-Hexyl cyclohexane	−7.299	569.8	129.4	0.011	202–293
Isobutyl chloride	−6.938	369.2	86.2	0.024	130–203
Isoamyl bromide	−5.965	254.3	119.8	0.021	161–239
tert-Butyl benzene	−6.892	401.1	131.1	0.006	200–263
n-Propanol[b]	−8.022	937.6	76.5	0.045	148–243
n-Propanol[c]	−6.964	692.4	89.2	0.078	138–170
Glycerol[c,d]	−13.132	2738.7	118.3	0.029	231–303
Ethanol[c,e]	−7.656	791.6	59.7	0.120	124–273
"Low"-temperature region					
cis-hept-2-ene	−9.473	504.2	82.3	0.016	119–136
Isobutyl chloride[f]	−14.654	921.0	70.5	0.051	99–115
Isoamyl bromide[f]	−19.270	1724.6	69.4	0.099	113–137
Ethyl cyclohexane	−10.855	839.4	81.2	0.010	130–144
sec-Butyl cyclohexane	−9.556	726.7	111.0	0.008	160–176
Isopropyl cyclohexane[g]	...	...	...	...	159–166

[a] RMSE is the root-mean-square error, $[n^{-1}\{\Sigma_n(\ln\eta_{obs} - \ln\eta_{calc})^2\}]^{1/2}$, where n is the number of observations.

[b] T. Lyon and T. A. Litovitz, J. Appl. Phys. 27, 179 (1956).

[c] Reference 3.

[d] R. Piccirelli and T. A. Litovitz, J. Acoust. Soc. Am. 29, 1009 (1957).

[e] S. Mitsukuri and T. Tonomura, Proc. Acad. Sci. Tokyo 5, 23 (1929).

[f] D. J. Denney, J. Chem. Phys. 30, 159 (1959).

[g] Available temperature range too small to define A'', B'', and T_0.

liquid were cooled to a glass at 77°K, and then heated at a rate of about 2°/min. Most of the liquids showed no tendency to crystallize during the few minutes required for this cooling, although some required to be cooled directly in liquid nitrogen to prevent crystallization. Powdered glass was used as a reference material for the DTA because of the large temperature range involved. The glass-transition temperature was taken at the intersection of straight lines drawn through the initial base line and the subsequent sloping portion of the curve.[5] The values of T_g quoted are the mean of at least three observations, and are estimated to be accurate to ±2°. T_g was found to be independent of heating rates between 1°–10°/min. There was no indication of subsidiary T_g's at lower temperatures as have been found in polymers[6] and postulated in simple liquids.[7]

[5] E. V. Thompson, J. Polymer Sci. Pt. A 4, 199 (1966).

[6] A. H. Willbourn, Trans. Faraday Soc. 54, 717 (1958).

[7] K. H. Illers, Rheol. Acta 3, 185 (1964).

Viscosities were measured in capillary viscometers to an accuracy of ±0.5% at temperatures maintained constant to ±0.05° as described previously.[2] The constants in Eq. (1) were determined by a least-mean-squares procedure using a digital computer.

The aromatic hydrocarbons and esters were the same samples as were used in the previous viscosity studies. The other hydrocarbons and the alkyl halides were dried with anhydrous potassium carbonate and fractionally distilled, while the alcohols were dried with anhydrous calcium sulfate.

Table I contains the constants in Eq. (1) obtained from the measured viscosities with the root-mean-square error in the fit. Both Eq. (1) and a plot of $\log\eta$ against $(1000/T)^4$ were used to search for a change in viscosity behavior in the non-Arrhenius region.[2] This has been found in the liquids in Table II in addition to those reported previously.[2]

The observed values of T_g are shown in Table III along with the values predicted from Eq. (1).

III. DISCUSSION

A. Comparison of Observed T_g's with the Results of Other Workers

The glass-transition temperatures of the three alcohols in Table III have been investigated by other workers. From specific-heat measurements by Parks[8] and by Kelley,[9] T_g of ethanol has been shown to lie in the range 92°–96°K and 93°–97°K, respectively. Similar studies show T_g of n-propanol[10] to lie between 93° and 100°K and T_g of glycerol[11] between 180° and 189°K. Glycerol has also been studied by DTA [12] and T_g was found to occur at 187°K. Table III shows that the results obtained in this investigation are consistent with those previous values.

B. Comparison of Observed T_g's with Those Predicted from Viscosity Measurements

It is convenient to consider two classes of liquids, those which have a change in their viscous behavior in the non-Arrhenius region and those which exhibit no such change in the experimentally accessible region.

The 14 liquids in Sec. A of Table III have two non-Arrhenius viscosity regions, and Eq. (1) must be applied in two separate temperature regions with two different sets of values of the constants A'', B'', and T_0. It is likely that this changeover from one non-Arrhenius region to another occurs when molecular rotation becomes restricted on the time scale of the translational relaxation time.[4] This implies that only one form of a liquid can exist at a given temperature, and so the observed values of T_g should correspond to those predicted by the "low"-temperature form of the T_0 equation and not the "high"-temperature form. Agreement between measured and predicted "low" T_g values is good for nine of the liquids in Table III. There is less satisfactory agreement for n-propyl benzene, di-i-butyl phthalate, and s-butyl cyclohexane, possibly

because of small inaccuracies in the viscosity data. Agreement is poor for dimethyl phthalate and i-propyl cyclohexane because the viscosity in the "low"-temperature form could be measured only over a small temperature range before crystallization occurred.

The remaining 20 liquids in Table III show no observable change in their viscous behavior in the experimentally accessible region, and Eq. (1) with one set of constants A'', B'', and T_0 has been used to predict T_g. Agreement between measured and predicted values of T_g is satisfactory for the seven liquids in Sec. B. The differences between the T_g values for the 10

TABLE III. Comparison of observed and calculated glass transition temperatures T_g.

Liquid	"High" T_g (°K)	"Low" T_g (°K)	Observed T_g (°K)
Section A			
n-Propyl benzene	129.9	126.9	122
Isopropyl benzene	130.4	123.7	125
n-Butyl benzene	127.5	125.2	125
sec-Butyl benzene	140.1	128.0	127
n-Pentyl benzene	144.9	128.9	128
Isobutyl chloride	96.2	91.1	88
Isobutyl bromide	104.2	98.7	95
Isoamyl bromide	121.9	104.4	105
Dimethyl phthalate	210.7	206.0	193
Di-isobutyl phthalate	209.4	183.0	188
Ethyl cyclohexane	106.9	101.8	98
Isopropyl cyclohexane	123.1	<123.1	108
sec-butyl cyclohexane	138.2	129.4	123
cis-Hept-2-ene	100.5	95.0	93
Section B			
Toluene	114.1	⋯	113
Ethyl benzene	111.8	⋯	111
$tert$-Butyl benzene	142.0	⋯	142
Di-n-butyl phthalate	176.5	⋯	176
Di-(2-ethyl hexyl) phthalate	183.7	⋯	184
n-Propanol	105.8[a] or 101.2[b]	⋯	98
Glycerol	181.9	⋯	186
Section C			
Ethanol	80.8	⋯	96
n-Hexyl benzene	144.8	⋯	137
Methyl cyclohexane	90.6	⋯	85
n-Butyl cyclohexane	133.5	⋯	119
n-Pentyl cyclohexane	143.3	⋯	125
n-Hexyl cyclohexane	144.7	⋯	133
Hex-1-ene	92.6	⋯	≤83
$trans$-Hex-2-ene	96.0	⋯	85
Hept-1-ene	103.0	⋯	91
cis-Oct-2-ene	112.5	⋯	101
Section D			
Pent-1-ene	80.9	⋯	<83
cis-Pent-2-ene	80.0	⋯	<83
$trans$-Pent-2-ene	79.7	⋯	<83

[a] Reference 3.
[b] Table II, Ref. b.

TABLE II. Melting points and intersection temperatures.[a]

Liquid	T_M(°K)	T_K(°K)
Ethyl cyclohexane	161.9	148
Isopropyl cyclohexane	183.8	~165
sec-Butyl cyclohexane	⋯	182
cis-Hept-2-ene	⋯	139
Isoamyl bromide	161.3	155
Isobutyl chloride	142.0	122

[a] Approximate temperature at which change in non-Arrhenius viscosity behavior occurs.[3]

[8] G. S. Parks, J. Am. Chem. Soc. **47**, 338 (1925).
[9] K. K. Kelley, J. Am. Chem. Soc. **51**, 779 (1929).
[10] G. S. Parks and H. M. Huffman, J. Phys. Chem. **31**, 1842 (1927).
[11] G. E. Gibson and W. F. Giauque, J. Am. Chem. Soc. **45**, 393 (1923).
[12] J. A. McMillan, J. Chem. Phys. **42**, 3497 (1965).

liquids in Sec. C are too large to be caused by experimental errors except in the case of ethanol where the discrepancy may be caused by unreliable viscosity data. The values of T_g of the three pentenes in Sec. D are too low to be measured with the available apparatus.

Apart from ethanol, each of the substances showing this discrepancy slowly crystallized at temperatures some 10° or 20° below the normal freezing point when the viscosity was typically about 1P. It is significant that several substances of similar molecular structures (such as s-butyl cyclohexane and cis-hept-2-ene) which could be supercooled to higher viscosities without crystallization exhibited a change in viscosity behavior at temperatures at or below the melting point. In each case the T_0 and T_g of the lower temperature form of the substance is lower than that of the higher-temperature form of the substance: for some liquids the difference between the two T_g's is small (e.g., 2° in n-butyl benzene) while in other liquids the difference is large (e.g., 16° in n-pentyl benzene).

This suggests that if the viscosities of these substances could be measured at lower temperatures without crystallization occurring, then a change in non-Arrhenius viscosity behavior would be observed. The measured T_g, obtained after rapid cooling of the liquid, corresponds to the lower-temperature form of the liquid, and this T_g is lower than that predicted from studies of the viscosity of the high-temperature form.

There remain, however, the seven liquids in Sec. B of Table III which have only one observable non-Arrhenius region and for which there is good agreement between the observed and predicted T_g values. There are two possibilities which could account for this agreement. One is that these substances have only one non-Arrhenius region in the liquid range, so that at T_0 the molecules are still able to rotate about one molecular axis. The other possibility is that such substances do indeed have two non-Arrhenius regions, but that the T_g values of the two forms of the liquid are within a few degrees of each other and so are indistinguishable experimentally. It is difficult to distinguish between these possibilities. It is well known[13] that even at the melting point of solids such as toluene or ethanol no molecular rotation occurs in the crystalline solid. The volume available to a molecule in the equilibrium glassy liquid at T_0 is slightly greater than in the solid at the same temperature. If this volume difference is sufficient to permit molecular rotation about one axis at T_0, then only one non-Arrhenius region would be expected, and observed T_g values would agree with those predicted. On the other hand, if there is still insufficient volume for molecular rotation at T_0, then a change in non-Arrhenius viscosity behavior must have occurred at

some temperature higher than T_0 and probably higher than T_g: If this temperature is not far above T_g, then the T_g values for the two forms of the liquid would be indistinguishable experimentally.

We conclude that the glass-transition temperatures observed in most liquids correspond to the lower-temperature form of the liquid in which molecular rotation occurs only as a result of molecular translational motion. These T_g values can be predicted from viscosity data only when sufficient data are available at low temperatures.

This use of the T_0 equation to predict T_g agrees with the conclusions of Miller[14] that the equation may be used to calculate T_g of polystyrene and polyisobutylene. It confirms that T_g is primarily an "iso-viscous" and not an "iso-free-volume" condition.[2,14]

C. Application of the T_0 Equation to Experimental Viscosity Data

The present results show that reliable values of T_g (and by implication T_0) may be estimated from Eq. (1) when it is applied only in the appropriate non-Arrhenius temperature range. Attempts to apply this equation throughout the liquid range including the Arrhenius region do not give a good description of the experimental data, and the resultant T_g values are substantially lower than those observed and are dependent on the particular temperature region chosen. This explains the irregularities found by Lewis[15] in the T_0 values of the n-alkanes. When only the non-Arrhenius region is considered, the resultant B'' and T_0 values of the n-alkanes increase smoothly with increasing molecular weight, while the constant A'' is essentially independent of molecular weight.

IV. CONCLUSIONS

We conclude that the glass-transition temperature in liquids occurs when the viscosity of the liquid reaches 10^{13} P. T_g may be predicted from studies of the temperature dependence of the viscosity by means of Eq. (1) provided that precise viscosity data are available over a reasonably wide range of temperature or viscosity for the lower-temperature non-Arrhenius region of the liquid. If viscosity data are available only in the higher-temperature non-Arrhenius region, observed values of T_g are usually lower than those predicted by Eq. (1) on account of a change in non-Arrhenius viscosity behavior at lower temperatures where viscosity cannot be measured because of crystallization of the liquid.

[13] J. Timmermans, J. Phys. Chem. Solids **18**, 1 (1961).

[14] A. A. Miller, J. Polymer Sci. Pt. A **2**, 1095 (1964).
[15] O. G. Lewis, J. Chem. Phys. **43**, 2693 (1965).