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Viscosity-Temperature Function for Sorbitol from Combined Viscosity and Differential Scanning Calorimetry Studies

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Viscometry and scan rate dependent heat capacity measurements have been performed on the polyalcohol sorbitol which has recently been useful as a solvent for various spectroscopic studies. The present measurements establish that the relaxation time characteristics of this multilaterally hydrogen-bonded liquid follows the VTF equation over some 11 orders of magnitude in the relaxation time.

Because of its convenient glass transition temperature, $T_g = -9^\circ\text{C}$, and solvent properties, the hydrogen-bonded liquid sorbitol ($\text{C}_6\text{H}_8(\text{OH})_6$) has recently proven very useful as a solvent for the study of the local structural relaxation in the vicinity of various optically active species in the glass transition region.¹ In order to properly interpret the spectroscopic observations it was necessary to know the temperature dependence of the solvent viscosity. In the present note we report the results of spindle viscometry studies which, together with information from variable heating rate differential scanning calorimetry experiments, seem to establish that this polyalcohol shows no tendency to return to Arrhenius behavior as frequently found for glass-forming liquids of high T_g , but instead conforms to a simple VTF-type viscosity-temperature relation²

$$\eta = A \exp[B/(T - T_0)] \quad (1)$$

or the slightly modified, theoretically preferable³ version

$$\eta = A' T^{1/2} \exp[B'/(T - T_0)] \quad (2)$$

(A , A' , B , and T_0 constants) over the entire viscosity range of 10 – 10^{13} cP between 90°C and T_g .

Experimental Section

The direct measurements were made with a Brookfield spindle viscometer, calibrated in the viscosity range 10 – 10^6 cP with standard viscosity oils (Cannon Co.). Sorbitol samples were taken from the same bottle of Matheson Cole and Bell material used in the optical probe relaxation studies. Sample temperatures were maintained within 0.01°C by means of a Haake constant temperature bath, the temperature of which was measured to 0.01°C by a Hewlett Packard quartz thermometer. Three different spindle sizes were used to cover three orders of magnitude in viscosity in the temperature range 100 – 35°C . The lower limit was set by the tendency of the sorbitol to crystallize during the long temperature equilibration periods.

To reach lower temperatures, and obtain information on the temperature dependence of the relaxation time in the very long relaxation time regime near the glass transition, we studied the enthalpy relaxation process using a differential scanning calorimeter. The work of Moynihan and co-workers⁴ has shown that the temperature depen-

dence of the enthalpy relaxation time, obtained from study of the C_p jump at T_g as a function of scanning rate, has the same value as that for the shear relaxation process (viscous flow). The DSC method has much appeal since one can work quickly with small samples in a regime where the viscosity itself has risen to values of the order of 10^{11} P and has become rather difficult to measure accurately.

In the DSC method, the rate of heat absorption of a small sample is monitored during heating at the same scan rates q ($0.2^\circ\text{C}/\text{min} \leq q \leq 20^\circ\text{C}/\text{min}$) used in the initial vitrification. Such scans can be analyzed with some difficulty to obtain enthalpy relaxation functions ϕ_H ,^{4,5} but to obtain the activation enthalpy for the relaxation process it is only necessary to construct an Arrhenius plot of \log -(scan rate) vs. $1/T_g$.⁴

T_g can be defined by different points on the C_p vs. T curve, as shown in Figure 1A. If the relaxation process has an Arrhenius temperature dependence, then ΔH_H will be independent of the point on the C_p scan chosen to define T_g . If, however, the relaxation process is non-Arrhenius then the value of ΔH_H (which will in this case be an average value over a small temperature interval) will depend on the point chosen to define T_g : points defined higher in temperature on the relaxation curve will yield lower (average) activation energies. The decreases should coincide with the decreasing apparent activation energy for viscosity. For both Arrhenius and non-Arrhenius cases, the treatment assumes that the isothermal enthalpy relaxation function has a temperature-independent form in the temperature range of study. This has so far proved to be the case.⁴

Results and Discussion

An Arrhenius plot of the spindle viscometry data is shown in Figure 1 (open circles). These data are fitted with a standard deviation of 1.5% by eq 1 with parameters $A = 1.90 \times 10^{-2}$ cP, $B = 1832$ K, $T_0 = 212$ K, and by eq 2 with parameters $A' = 4.068 \times 10^{-4}$ cP, $B = 2045$ K, $T_0 = 206$ K. Plots of eq 1 and 2 with these parameters, for temperatures in the range 250 – 373 K are shown in Figure 1 (solid line through solid circles).

Results of the different scan rate DSC experiments are shown in Figure 1B. The different T_g points, defined T_{g1} and T_{g2} as shown in Figure 1A, span different temperature ranges, so that if eq 1 continues to describe the viscosity in the temperature range around T_g , then the slopes of the T_{g1} and T_{g2} Arrhenius plots should be different. This proves to be the case. Because of uncertainties in locating the T_g points in different scans and also the limited temperature range covered, the (average) activation energies

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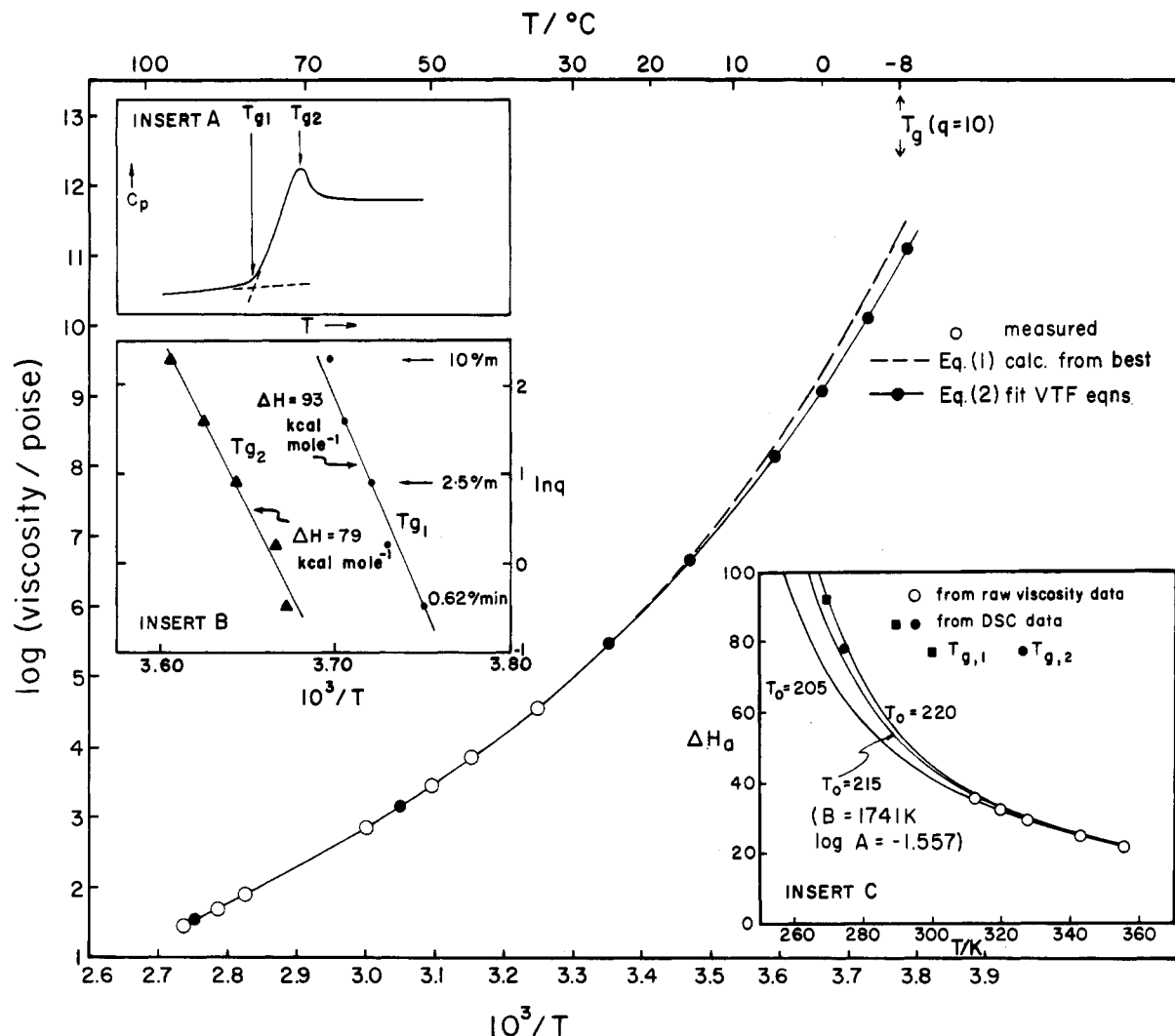


Figure 1. Arrhenius plot of viscosity in poise for *d*-sorbitol, and extrapolations to lower temperatures by using best-fit parameters for eq 1 and 2. (A) Schematic of sorbitol heat capacity through the glass transition showing definition of points T_{g1} and T_{g2} . (B) Plots of $\ln q$ (heating rate) vs. $1/T_0$ for the different T_0 definitions, showing activation energies for enthalpy relaxation dependent on temperature range. (C) Plots of apparent activation energy for viscosity vs. temperature from equation best fitting the viscosity data subject to predetermined T_0 values. Accord with activation energies from enthalpy relaxation data is best for $T_0 = 118$ K.

are not definable to better than ± 5 kcal mol $^{-1}$ by the DSC method. The values obtained, 79 ± 5 and 93 ± 5 kcal mol at 267 and 273 K, respectively, are higher than those predicted by the best-fit VTF equation parameters by amounts which exceed the uncertainty limits, indicating that a somewhat higher value of T_0 applies near T_g . This is a significant observation, since the general finding for viscous liquids is that they tend to deviate from eq 1 in the opposite direction near T_g , i.e., the relaxation processes usually return to Arrhenius behavior for $T \rightarrow T_g$.^{6,7}

The DSC data are consistent with a VTF equation in which T_0 has a value 10–15 °C higher than the viscosity best fit value, as shown in Figure 1C. This shows the variations in activation energy predicted by VTF equations which best fit the viscosity data subject to preselected T_0 values of 205, 215, and 220 K. The two DSC-derived values are shown as solid symbols, while values derived from pairs of viscosity data points separated by 20 °C or more are shown as open circles. It is clear that viscosity data of the present range and accuracy cannot distinguish between the alternative T_0 values with the sensitivity which the DSC

data possess by virtue of their closer proximity to T_0 .

It seems reasonable to conclude the following:

(1) The viscosity of sorbitol can be well represented over the whole range of temperatures between the fusion temperature and the glass transition temperature, corresponding to some 13 orders of magnitude in relaxation time, by eq 1 with parameters $T_0 = 215$, $B = 1741$, and $\log A = -1.557$.

(2) This unusually wide range of eq 1 behavior, which contrasts with that of most molecular liquids,^{6,7} may be a common property of polyalcohols since the two earlier examples of such behavior are glycerol^{8,9} and butanediol.¹⁰ Fits to eq 1 (actually to the equivalent WLF equation) over a wide range of relaxation times were originally observed for polymers and polymer solutions.¹¹ It may be of significance that in both polyalcohol and polymer cases, T_g exceeds the Kauzmann temperature (determined from entropy extrapolation at the point where $S(\text{liq}) \rightarrow S(\text{cryst})$) by some 30%, whereas it is in the region $T/T_K \approx T/T_0 <$

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1.4 that the failure of eq 1 is usually observed. Kauzmann temperatures for sorbitol isomers will be reported separately.¹²

(3) In combination with standard viscometry in the low-to-medium viscosity range, the DSC method for characterizing the low temperature, high viscosity, activation energy may provide a simple method for examining the question of eq 1 adequacy near T_g for a range of substances.

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Multicomponent Diffusion of Polyelectrolyte Solutions with Added Simple Salt

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Diffusion coefficients are reported for dilute aqueous sodium poly(styrenesulfonate) and for two compositions of the ternary system sodium poly(styrenesulfonate)/sodium chloride/water at 25 °C. The conductimetric technique was used. The ternary diffusion data for the polyelectrolyte solution with added salt can be qualitatively predicted from binary transport data. As a result of electrostatic interaction between ions, diffusive flows of polyelectrolyte and added salt are strongly coupled.

Introduction

Multicomponent diffusion coefficients of strong electrolyte mixtures can be reliably predicted at low ionic strength from limiting ionic mobilities.¹⁻⁷ Because pure diffusion of electrolytes is characterized by zero flow of electric current, an electrolyte concentration gradient is accompanied by a gradient of electric potential that acts to increase the diffusion velocity of the less mobile ion and decrease the diffusion velocity of the more mobile ion.⁸ In a mixed electrolyte solution the electric potential gradient along a concentration gradient of one electrolyte sets in motion coupled flows of ions belonging to other electrolytes. In such systems strong interactions between diffusive flows may be anticipated whenever the ions have widely different mobilities. For example, the cross-diffusion coefficients of aqueous strong electrolyte mixtures containing acids (where the mobility of H^+ is large compared to the mobilities of other ions) can be as large as or even several times larger than main diffusion coefficients.^{6,7,9-11}

Polyelectrolyte solutions with added salt also exhibit strong coupling between diffusive flows.¹² The suggestion has been made that the large difference in mobility between polyion and counterions could result in cross-diffusion coefficients coupling flows of simple salt to polyelectrolyte flows that are orders of magnitude larger than the main diffusion coefficients.^{7,11} In this note some ternary diffusion measurements are reported which lend support to this claim. It is shown that the large coupling coefficients can be qualitatively predicted from binary transport data.

Experimental Section

Diffusion of sodium poly(styrenesulfonate) (NaPSSA)/sodium chloride/water was measured at 25 °C. This system has been well studied: transference,¹³ conduc-

TABLE I: Binary Diffusion Coefficient of Aqueous NaPSSA at 25 °C

$10^3 N_1 /$ (equiv/L)	$10^5 D /$ (cm ² /s)	$10^3 N_1 /$ (equiv/L)	$10^5 D /$ (cm ² /s)
4.03	0.534	13.0	0.562
7.25	0.550	17.0	0.562
10.0	0.557		

tance,^{14,15} emf,¹⁶ and diffusion (binary¹⁷ and tracer^{18,19}) data are available. Because of the low concentrations involved, the conductimetric technique was used. The equipment, the procedure, and the method of data analysis for the conductimetric determination of ternary diffusion coefficients have been described.^{6,7,11}

NaPSSA with 100% sulfonation and molecular weight

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