

Saturated Liquid Specific Heats of Ethylene Glycol Homologues

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Specific heats of the saturated liquid of the ethylene glycol homologues, mono- through pentaethylene glycol, have been determined by differential scanning calorimetry. Temperatures of the experiments ranged from 25 °C to the normal boiling points or to the onset of decomposition. High-temperature data are nonexistent for these compounds excepting monoethylene glycol where data can be found to 195 °C; no published specific heat values could be located for tetra- and pentaethylene glycol. Interesting phenomena were observed at high temperatures where changes in slope occurred in the specific heat-temperature curves. A number of exploratory studies were made to find some reasonable explanation for this behavior. The conclusion is that this phenomenon is attributable to intramolecular hydrogen bonding effects.

Introduction

Specific heats of the saturated liquid of the ethylene glycols, mono-, di-, tri-, tetra-, and penta-, are important in industry and are of academic interest. Literature sources for experimental specific heats are rather sparse. Touloukian (1) has collected and correlated several sets of data for ethylene glycol to 195 °C which are reported in a volume of the TPRC Data Series. In Dow's sales booklet "Glycols, Properties and Uses", data are listed for mono-, di-, and triethylene glycol from 15.6 to 115.5 °C. No information could be located for tetra- and pentaethylene glycol.

Experimental Section

The measurements reported here were made by a Perkin-Elmer Differential Scanning Calorimeter-2 which we have found to be an efficient and a highly accurate means to obtain specific heat data over extended temperature ranges. Liquid specific heats were measured by usual procedures. At a selected temperature range, programmed scanning rate (10°/min), and sensitivity (10 mcal/s), a sapphire standard is first scanned and an empty pan, blank, baseline is established. The sample is hermetically sealed in a nitrogen atmosphere in the same volatile pan used for the standard and blank scans and is subsequently scanned at the exact same conditions. Sample sizes were used so that the volume fractions of the vapor phase would be 0.0005–0.001. To cover a temperature range of 25 to 250 °C, three to four separate overlapping runs are made each with fresh material and scanned in duplicate. This is purely arbitrary but experience has proven that this procedure is best for the most accurate data and readily shows up any discontinuities—real or otherwise. Otherwise could be due to inadvertently not placing the cell covers in exact positions or the point is reached when the cells need to be cleaned and reconditioned. Impurities in samples can also cause problems. Gold sample pans were used; a reaction of the aluminum pans and the hydroxyl compounds was evident.

Table I. Ethylene Glycol Homologues Saturated Liquid Specific Heat-Temperature Data

temp, °C	specific heat, cal/(g °C)				
	mono	di	tri	tetra	penta
0	0.543	0.529	0.498	0.495	0.505
20	0.569	0.547	0.517	0.512	0.515
40	0.594	0.565	0.536	0.531	0.525
60	0.618	0.583	0.555	0.547	0.535
80	0.642	0.601	0.574	0.562	0.545
100	0.665	0.619	0.593	0.577	0.555
120	0.688	0.637	0.612	0.590	0.565
140	0.710	0.655	0.631	0.603	0.575
160	0.732	0.673	0.650	0.614	0.585
168			0.658		
178		0.690			
180	0.753	0.691	0.662	0.625	0.595
190	0.763				
200	0.774	0.696	0.666	0.635	0.605
210	0.784				
215	0.789				
220	0.792	0.703	0.669	0.643	0.615
240		0.710	0.673	0.651	0.624
260			0.677	0.658	
std dev	0.0048	0.0041	0.0032	0.0035	0.0039

The DSC is actually measuring liquid specific heats at saturation (C_s). Values at temperature, t °C, are calculated by the DSC scans relationships:

$$C_s = \left[\frac{\text{amplitude (sample)}}{\text{amplitude (sapphire)}} \right] \times \left[\frac{\text{weight (sapphire)}}{\text{weight (sample)}} \right] \times [\text{specific heat (sapphire)}]$$

The amplitudes (distance from an isothermal baseline to a point on the DSC curve) of the sapphire and sample are adjusted by appropriate addition or subtraction of the no sample baseline amplitude.

The instrument used here is on-line to a Control Data Corp. 1700 computer so specific heat calculations for each degree of temperature are easily obtained. Also, the data are fitted and smoothed by a polynomial regression analysis program with standard deviation, percent difference of experimental to calculated, and constants of first-, second-, and third-order equations listed.

The glycols used were Union Carbide Corp.'s highly refined materials. Gas chromatographic analyses indicated 99.9+ % purities with the exception of pentaethylene glycol which was 99.1% pure.

Results

Specific heat data measured as a function of temperature for the saturated liquid of five ethylene glycol homologues are listed in Table I. These are smoothed values; computer-calculated standard deviations for each set of experimental points are noted. The specific heat curves are shown in Figure 1. Also, the mono-, di-, and triethylene glycol data reported by Touloukian and Dow (2) are indicated.

Changes of slope in the di- and triethylene glycols curves are easily detected and are less pronounced in the mono- and tetraethylene glycol curves. Pentaethylene glycol exhibits no

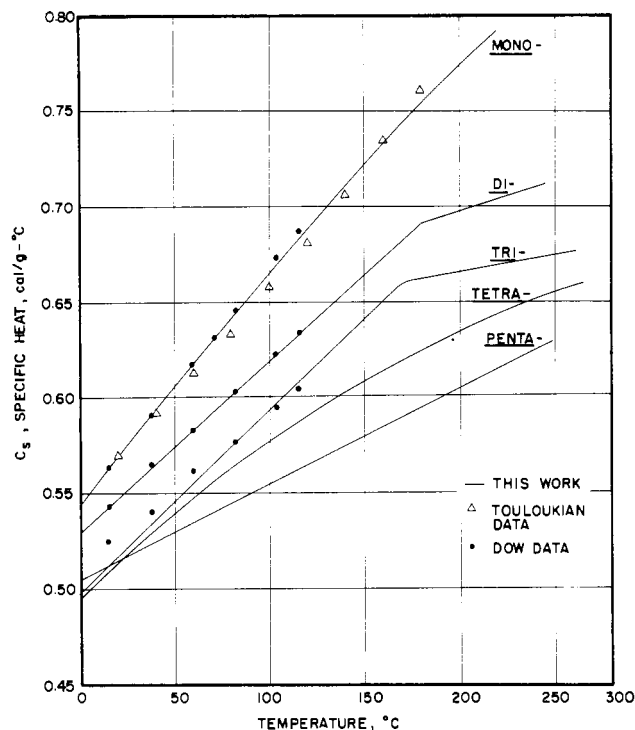


Figure 1. Ethylene glycol homologues, saturated liquid specific heat-temperature data.

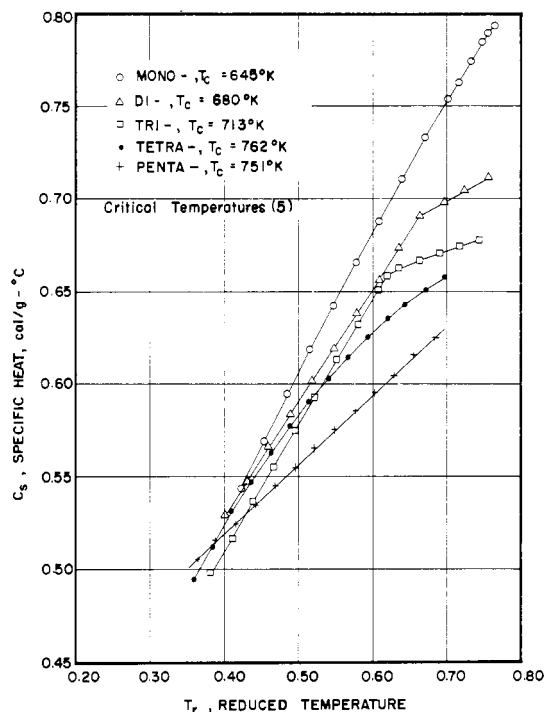


Figure 2. Ethylene glycols, specific heat vs. reduced temperature.

slope change over the temperature range studied. The temperatures at the point of the slope changes and reduced temperature values are as follows: ethylene glycol, 210 °C, $T_r = 0.75$; diethylene glycol, 178 °C, $T_r = 0.67$; triethylene glycol, 168 °C, $T_r = 0.62$; tetraethylene glycol, 160 °C, $T_r = 0.57$; pentaethylene glycol, —. The reduced temperature plots are given in Figure 2. Triethylene glycol was used for reproducibility tests where five DSC specific heat runs were made

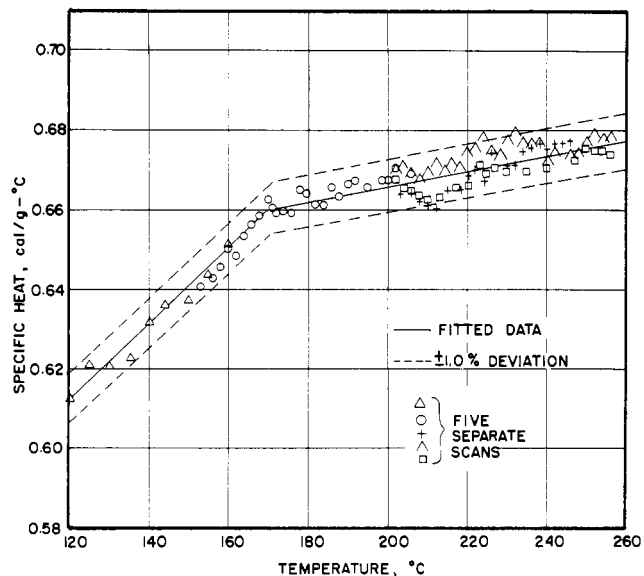


Figure 3. Experimental specific heat data for triethylene glycol.

covering various temperature ranges through and around the slope change point. The reproducibility was excellent as shown in Figure 3. Here actual experimental points are plotted with the fitted data reported in Table I and Figure 1; most points deviated by no more than 0.1–0.3%. This graph clearly defines the curve's slope change point.

Some analytical tests were made on triethylene glycol to check for thermal decomposition products where heats of reaction would influence specific heat data. Materials subjected to high temperatures in the DSC runs were analyzed by gas chromatography. Nothing significant was disclosed in this study except an increase of acetaldehyde from 36 to 77 ppm. The heat of reaction of acetaldehyde is endothermic which would give higher values and increase the slope of a specific heat curve. A mass spectroscopy pyrolysis test at 250 °C showed no evidence of decomposition products. Infrared scans of the original and multiheated material were made with only the appearance of acetaldehyde, very minute intensity, detected; a bonded OH band was present in the scan.

Thermal decomposition reactions have been ruled out as a cause for the changes in slope of the specific heat curves. Intramolecular hydrogen bonding appears precedent. The observed phenomena must indicate temperature-dependent disruption of the bonding with conversion to a monomeric form or to some monomeric/polymeric equilibrium condition. Some intramolecular hydrogen bonding studies by IR and NMR on ethylene glycol and related glycol compounds have been found in the literature; however, these were done on dilute solutions and at limited temperatures. Krueger and Mettee (3) and Prabhumeraski (4) have indicated intramolecular bonding as a possible explanation for the results obtained here.

Literature Cited

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- (2) The Dow Chemical Co., "Glycols, Properties and Uses", Midland, Mich., 1961.
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