Vaporization Enthalpies of the α,ω-Alkanediols by Correlation Gas Chromatography

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The vaporization enthalpies of 1,2-ethanediol through 1,10-decanediol, 1,12-dodecanediol, 1,14-tetradecanediol, 1,16-hexadecanediol, 1,4-butynediol, 2,5-dimethyl-3-hexyne-2,5-diol, and 2,5-dimethyl-3-hexane-2,5-diol are examined by correlation gas chromatography. A good correlation is observed between the mean literature values and the enthalpies of transfer from solution to the gas phase for all the α,ω-alkanediols examined. Intramolecular hydrogen bonding in the liquid phase of the smaller 1,ω-alkanediols does not appear to be very important thermochemically and appears to have a minimal effect in the gas phase as judged by the vaporization enthalpies of 1,4-butynediol, 1,4-butanediol, 2,5-dimethyl-3-hexyne-2,5-diol, and 2,5-dimethylhexane-2,5-diol. The sublimation enthalpies of the α,ω-alkanediols were calculated as the sum of the fusion and vaporization enthalpies at $T = 298.15$ K.

Introduction

The α,ω-alkanediols are important commercial products whose applications range from use as anti-freeze agents to uses as intermediates in the synthesis of polyesters. Many of their thermochemical properties have been reported in the literature. An important aspect that affects many of their properties is their ability to form intramolecular hydrogen bonds both in the condensed phase and in the gas phase. Two distinct hydroxyl frequencies are observed in the gas phase infrared region of 1,3-propanediol at approximately 3670 cm^{-1} and 3600 cm^{-1} at 498 K. Gaseous 1,4-butanediol also shows two stretching frequencies, but the lower frequency is considerably weaker. 1,5-Pentanediol through 1,8-octanediol exhibit only a single stretching frequency at approximately 3670 cm^{-1} at temperatures of $T = 498$ K and above.[1] The stretching frequency at 3670 cm^{-1} appears characteristic of a free hydroxyl group while the broader band at approximately 3600 cm^{-1} is more characteristic of a hydroxyl group that is hydrogen-bonded. 1,2-Ethanediol and other similar 1,2-diols show a single slightly broader stretching frequency shifted slightly from 3670 cm^{-1} to approximately 3650 cm^{-1}. Results from ab initio quantum mechanical calculations performed by Klein[2−4] have questioned whether these small spectroscopic shifts observed in IR and similar ones in NMR spectra are consequences of intramolecular hydrogen bonding in vicinol diols. According to Klein's calculations, other interactions, such as van der Waals dispersion forces or induced dipole/dipole interactions may be responsible for these small shifts.

The presence or absence of intramolecular hydrogen bonding in the gas phase can have substantial consequences on a compound's thermodynamic properties. The vaporization enthalpies of the α,ω-alkanedioic acids, for example, increase linearly with the number of methylene groups up to 1,10-decanedioic acids and then the increase begins to fall off. This result has been interpreted as a consequence of intramolecular hydrogen bond formation once the size of the ring increases sufficiently to accommodate the hydrogen-bonding characteristic of carboxylic acid dimers.[5,6] As expected, the vaporization enthalpies measured for those diacids that can form intramolecular cyclic acid dimers appeared to be temperature dependent, increasing at the higher temperatures. The increase was interpreted as resulting from an equilibrium between an acyclic and a cyclic form, with the latter form characterized by an unfavorable entropy term.

The α,ω-alkanediols also have a similar capacity to form intramolecular hydrogen bonds, although with different geometric constraints. We have been interested in examining what effect, if any, the formation of an intramolecular hydrogen bond in the gas phase as suggested by infrared studies has on the thermochemical properties of this series of compounds. Vapor pressures and vaporization or sublimation enthalpies of a number of α,ω-alkanediols have been reported by a number of research laboratories. Most of the results of these investigations have been reported at different temperatures. When adjusted to $T = 298.15$ K, a comparison of the results of some of these measurements show significant dispersion. To avoid discrepancies arising from the use of different algorithms to adjust values to $T = 298.15$ K, all experimental measurements were adjusted to $T = 298.15$ K using[7]

$$\Delta_l{}^gH^o{}_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = \Delta_l{}^gH^o(T_m) + (10.58 + 0.26C_{pl})(T_m - 298.15)/1000 \quad (1)$$

The term $\Delta_l{}^gH^o{}_m(T_m)$ represents the experimental vaporization enthalpy at the mean temperature of measurement, T_m; C_{pl} represents the estimated heat capacity of the diol at $T = 298.15$ K.[8] Literature vaporization enthalpies of the α,ω-alkanediols, the mean temperature of measurement, T_m, the molar heat capacity values, C_{pl}, used in conjunction with eq 1, and the adjusted vaporization enthalpies, are tabulated in Table 1. The vaporization enthalpies of 1,6-hexanediol, 1,8-octanediol, and 1,10-decanediol were also calculated from differences in the experimental sublimation and fusion enthalpies given in Table

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Table 1. Literature Vaporization Enthalpies of the α,ω-Alkanediols[a]

	$\Delta_l^g H_m(T_m)$ kJ·mol^{-1}	T_m K	C_{pl} J·mol^{-1}·K^{-1}	$\Delta_l^g H_m$(298.15 K) kJ·mol^{-1}	ref
1,2-ethanediol	56.0 ± 1.3	439	170	63.7 ± 3.6	9
	61.1	383	170	65.8 ± 2.0	10
	57.3	437	170	64.9 ± 2.6	10
	57.0	388	170	61.9 ± 2.2	11
	59.4 ± 0.6	347	170	63.5 ± 1.9	12
	57.4 ± 1.2	385	170	62.2 ± 2.4	13
	64.0	338	170	66.2 ± 1	14
	65.6 ± 0.6	298	170	65.6 ± 0.6	15
1,3-propanediol	63.3	408	201.9	70.2 ± 2.0	10
	72.4 ± 0.6	298	201.9	72.4 ± 0.6	15
	57.8	431	201.9	66.1 ± 3.2	11
	57.6 ± 0.6	393	201.9	63.6 ± 2.4	12
	60.4	461	201.9	70.6 ± 2.6	10
1,4-butanediol	62.3 ± 0.8	455	233.8	73.5 ± 3.8	9
	79.3 ± 1.0	298	233.8	79.3 ± 1.0	15
	78.3 ± 0.6	298	233.8	78.3 ± 0.6	16
1,5-pentanediol	64.9 ± 0.8	480	265.7	79.3 ± 4.4	9
	86.8 ± 1.0	298	265.7	86.8 ± 1.0	15
1,6-hexanediol	65.3 ± 1.4	488	297.6	82.0 ± 4.8	9
	90.7 ± 1.1[b]	298	297.6	90.7 ± 1.1	17
	87.0 ± 4.0	342	297.6	90.9 ± 4.1	18
	84.3 ± 1.0	380	297.6	91.5 ± 2.2	19
1,7-heptanediol	92.4 ± 3.0	341	329.5	96.5 ± 3.2	20
	93.8 ± 1.0	323	329.5	96.2 ± 1.2	17
1,8-octanediol	105.4 ± 1.8[b]	298	361.4	105.4 ± 1.8	17
	101.0 ± 1.7	356	361.4	107.0 ± 2.2	18
1,9-nonanediol	104.4 ± 6.8	360	393.3	111.4 ± 7.0	20
	110.0 ± 2.0	323	393.3	112.8 ± 2.1	17
1,10-decanediol	113.7 ± 2.1[b]	298	425.2	113.7 ± 2.1	17
	126.6 ± 4.2	298	425.2	126.6 ± 4.2	21
	112.4 ± 4.6	364	425.2	120.4 ± 4.9	18
1,11-undecanediol	123.0 ± 3.8	365	457.1	131.7 ± 4.1	20
1,12-dodecanediol	119.4 ± 5.4	379	489	130.5 ± 5.7	18
1,13-tridecanediol	122.0 ± 7.6	372	520.9	132.8 ± 7.8	20
1,14-tetradecanediol	128.1 ± 5.8	386	552.8	141.7 ± 6.2	18
1,15-pentadecanediol	124.3 ± 3.8	390	584.7	139.2 ± 4.4	20
1,16-hexadecanediol	130.4 ± 3.6	398	616.6	147.5 ± 4.3	18

[a] The vaporization enthalpy of the α,ω-alkanediols when necessary was adjusted to T = 298.15 K from the temperature of measurement using eq 1 and the estimated heat capacities of column 4.[8] Uncertainties in the first column are literature values. Uncertainties in the fifth column include uncertainties in temperature adjustments; [b] Calculated from the difference in $\Delta_{cr}^g H_m$(298 K) and $\Delta_{cr}^l H_m$(298 K) reported in Table 2.

Table 2. Sublimation and Fusion Enthalpies of Some α,ω-Alkanediols[a]

diol	$\Delta_{cr}^g H_m(T_m)$ kJ·mol^{-1}	T_m K	C_{pl}/C_{pcr} J·mol^{-1}·K^{-1}	$\Delta_{cr}^g H_m$(298 K) kJ·mol^{-1} [b]	$\Delta_{cr}^l H_m(T_{fus})$ kJ·mol^{-1}	T_{fus} K	$\Delta_{cr}^l H_m$(298 K) kJ·mol^{-1} [c]
1,6-hexanediol	112.0 ± 0.8	298	297.6/208.4	112.0 ± 0.8	22.2 ± 0.6	314.6	21.3 ± 0.7
1,8-octanediol	138.3 ± 1.6	323	361.4/262.2	139.3 ± 1.6	36.1 ± 0.4	332.7	33.9 ± 0.7
1,10-decanediol	149.8 ± 1.6	342	425.2/316	151.9 ± 1.7	41.7 ± 0.6	345.4	38.3 ± 1.2

[a] Ref 15. [b] Calculated from $\Delta_{cr}^g H^o_m(298\ \mathrm{K}) = \Delta_{cr}^g H^o_m(T_m) + (0.75\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}} + 0.15C_{pl})(T_m - 298.15)/1000$.[7] [c] Calculated from $\Delta_{cr}^l H^o_m(298\ \mathrm{K}) = \Delta_{cr}^l H^o_m(T_m) + [0.15C_{pcr} - 0.26C_{pl} - 9.83\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}](T_{fus} - 298.15\ \mathrm{K})/1000$, where C_{pcr} is the heat capacity of the crystal at T = 298.15 K.

2. Experimental sublimation and fusion enthalpies were both adjusted to T = 298.15 K using the equations given in the footnotes of Table 2.

Experimental vaporization enthalpies are plotted as a function of the number of carbon atoms in Figure 1. Although a significant amount of scatter exists in the data, averaging all the values results in a linear plot as illustrated in Figure 2 and summarized in Table 3. The solid line in the graph was calculated by a linear regression analysis of vaporization enthalpy as a function of the number of methylene groups, N, by ignoring the values of 1,11-undecanediol through 1,16-hexadecanediol and is represented by eq 2. The fit was characterized by a standard deviation of (± 1.1) kJ·mol^{-1}:

$$\Delta_l^g H^o_m(298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (7.10 \pm 0.15)N + (48.37 \pm 1.16) \quad r^2 = 0.9969, \quad (2)$$

In the condensed phase, these materials can hydrogen bond both by intermolecular and intramolecular processes. Gas phase infrared studies suggest that only 1,3-propanediol and, to a lesser extent, 1,4-butanediol have any propensity to form intramolecular hydrogen bonds at T = 498 K and above. The experimental vaporization enthalpies have been measured over a variety of temperatures. Since formation of an intramolecular hydrogen bond should be characterized by an unfavorable entropy term, vaporization enthalpies measured at the higher temperatures should result in larger numerical values than measurements on the same compounds at lower temperatures, once adjusted to T = 298.15 K, as observed in the diacids,[5,6] unless there is some compensating effect in the condensed phase. An examination of the vaporization enthalpies in Table 1 and the mean temperature at which they were measured does not reveal any obvious trends when the data are adjusted to T =

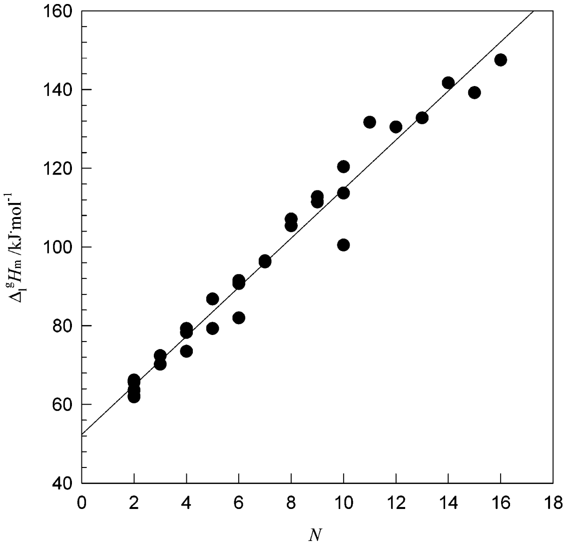

Figure 1. Experimental vaporization enthalpies of the α,ω-alkanediols in kJ·mol^{-1} as a function of the number of number of methylene groups, *N*. The equation of the line is given by $\Delta_l^g H^o_m$(298.15 K)/kJ·mol^{-1} = (6.24 ± 0.192)*N* + (52.37 ± 4.51), (r^2 = 0.9714).

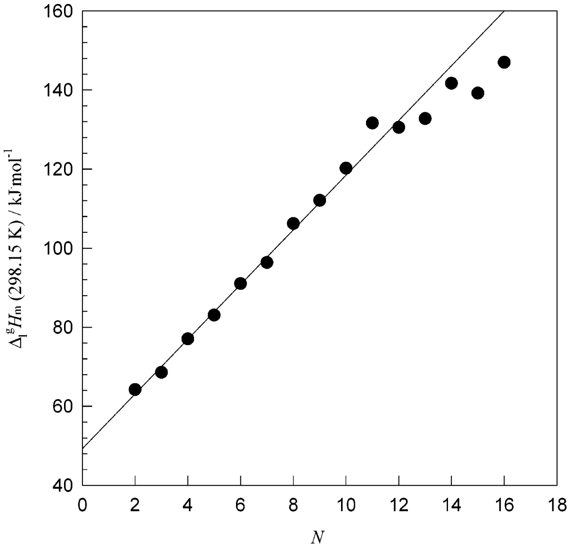

Figure 2. Averaged experimental vaporization enthalpies of the α,ω-alkanediols in kJ·mol^{-1} as a function of the number of methylene groups, *N*. The line was drawn considering the experimental vaporization enthalpies of the first nine members of the series.

298.15 K. The near linearity observed for the early members of the series, particularly 1,2-ethanediol through 1,6-hexanediol, suggests that either there is little effect of intramolecular hydrogen bonding on the vaporization enthalpies of these materials or that the effect is similar in all homologues.

One manner of testing whether the use of average values to represent the vaporization enthalpies of these compounds is a valid comparison, in this instance, is to examine the vaporization enthalpies of these materials by an independent method. It has been shown previously that correlation gas chromatography affords an excellent way of evaluating the vaporization enthalpies of homologous series.[22−25] The sensitivity of the flame ionization detector and the limited capacity of the capillary columns used in these experiments assures that the chromatograms are obtained under dilute conditions. While the extent to which the diols hydrogen bond to each other or to the column while adsorbed on the column is not known, the dilute conditions of the experiment are optimal to encourage intramolecular hydrogen bonding. These conditions are clearly different from measurements made on the pure materials. Thus it might be expected that values of the enthalpy of transfer from solution to the vapor, $\Delta_{sln}{}^g H^o_m$, might not correlate as well with $\Delta_l^g H^o_m$(298.15 K) for those compounds that do intramolecularly hydrogen bond in the gas phase.

Table 3. Average Experimental Vaporization Enthalpies at *T* = 298.15 K of α,ω-Alkanediols from C_2 to C_{10}

diol	$\Delta_l^g H_m$(298.15 K)[a] kJ·mol^{-1}
1,2-ethanediol	64.2 ± 1.2
1,3-propanediol	68.6 ± 3.2
1,4-butanediol	77.0 ± 3.6
1,5-pentanediol	83.1 ± 7.4
1,6-hexanediol	91.0 ± 5.2
1,7-heptanediol	96.4 ± 0.3
1,8-octanediol	106.2 ± 1.6
1,9-nonanediol	112.1 ± 1.4
1,10-decanediol	120.2 ± 7.5

[a] Uncertainties represent two standard errors of the mean, σ_m, and were calculated as follows: $\sigma_m = [1/n(n-1)\Sigma\delta_i^2]^{1/2}$ where $\Sigma\delta_i^2$ represents the sum of the square of δ of *n* measurements, and δ represents the difference of each measurement from the mean.

Experimental Section

The α,ω-alkanediols were all commercial samples and were used without any further purification. Each was analyzed by gas chromatography, and the mole fraction was found to be at least 98 % with the exception of 1,6-hexanediol, 1,7-heptanediol, and 2,5-dimethyl-3-hexane-2,5-diol. These were reported by the manufacturer to be 97 %, 95 %, and 97 % pure, respectively. Since the samples were analyzed as a mixture, other than for purposes of identity, sample purity is generally not a concern. Although not identified in this work, these impurities were separated by the columns and appeared as separate, small, resolved peaks in the chromatogram. Correlation gas chromatography experiments were performed over a period of time by several collaborators on several HP 5890A gas chromatographs. All were equipped with split/splitless capillary injection ports and flame ionization detectors (fid). All were run in split mode. All retention times were recorded to three significant figures following the decimal point. Some analyses were recorded on a HP 3989A Integrator. Others were obtained using HP GC Chemstation. All instruments were run isothermally using 30 m SPB-5 and DB-5 capillary columns. Helium was used as the carrier gas. At the higher temperatures, the retention times of the solvents, $CHCl_3$ and CH_3OH, were used to determine the dead volume of the column. The retention time of methane was used at the lower temperatures. Retention times of non-retained substances increase with increasing temperature. This is a consequence of the increase in viscosity of the carrier gas; it is the criterion used to confirm that these materials are not being retained on the column. Adjusted retention times, t_a, were calculated by subtracting the measured retention time of the non-retained reference from the retention time of each analyte as a function of temperature, generally over a 30 K range. Column temperatures were controlled by the gas chromatograph and were monitored independently by using a Fluke 51 K/J thermometer. Temperature was maintained constant by the gas chromatograph to ± 0.1 K.

The adjusted retention time of a compound, t_a, is inversely proportional to a compound's vapor pressure on the column. The slope of the line resulting from plotting the natural logarithm of the reciprocal adjusted retention time ($\ln(t_o/t_a)$), (where t_o =

Table 4. Summary of the Correlation of Enthalpies of Transfer versus Experimental Vaporization Enthalpies for 1,5-Pentanediol to 1,10-Decanediol

			$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(404 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1}	
mix 1	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1} = (1.889 ± 0.169)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(404 K) − (10321 ± 1226), (r^2 = 0.9937)					
1,5-pentanediol	4594.2	11.756	38194	83069	82452
1,6-hexanediol	5133.3	12.461	42676	91025	90916
1,7-heptanediol	5604.4	13.02	46593	96358	98312
1,8-octanediol	6029.5	13.474	50127	106236	104987
1,9-nonanediol	6504.6	14.076	54077	112092	112446
1,10-decanediol	6977.7	14.682	58010	120212	119874

Table 5. Summary of the Correlation of Enthalpies of Transfer versus Experimental Vaporization Enthalpies for 1,2-Ethanediol to 1,7-Heptanediol

			$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(362 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1}	
mix 2	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1} = (1.8736 ± 0.077)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(362 K) + (2163 ± 1036), (r^2 = 0.9949)					
1,2-ethanediol	4018.4	11.682	33407	64224	64756
1,3-propanediol	4312.1	11.52	35849		69330
1,4-butanediol	4796	12.046	39872	77045	76868
1,5-pentanediol	5174.9	12.393	43022	83069	82770
1,6-hexanediol	5626.8	12.933	46779	91025	89809
1,7-heptanediol	6121.6	13.595	50892	96358	97516
			$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(344 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1}	
mix 3	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/kJ·mol^{-1} = (1.384 ± 0.046)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(344 K) + (19431 ± 455), (r^2 = 0.9989)					
1,2-ethanediol	3882.9	11.359	32281	64225	64121
1,3-propanediol	4442.8	11.917	36936		70565
1,4-butanediol	5037.3	12.752	41878	77045	77407
1,5-pentanediol	5507	13.345	45783	83069	82813
			$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(356 K)	$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1}	
mix 4	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_{\mathrm{l}}{}^{\mathrm{g}}H_{\mathrm{m}}$(298.15 K)/J·mol^{-1} = (1.482 ± 0.102)$\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}$(356 K) + (17115 ± 1339), (r^2 = 0.9906)					
1.2-ethanediol	3767.8	11.303	31324	64225	63547
1,3-propanediol	4519.2	12.402	37571		72806
1,4-butanediol	4962.7	12.777	41258	77045	78272
1,5-pentanediol	5399.7	13.276	44891	83069	83657
1,6-hexanediol	5905.9	13.946	49099	91025	89895

1 min) against reciprocal temperature, measures the negative of the enthalpy of transfer from the column to the gas phase divided by the gas constant, ($-\Delta_{\mathrm{sln}}{}^{\mathrm{g}}H_{\mathrm{m}}/R$, $R = 8.314$ J·mol^{-1}·K^{-1}). Once calculated, the enthalpy of transfer is correlated with the vaporization enthalpies of a series of standards also included in the chromatographic analysis whose vaporization enthalpies are known. In this instance, the experimental averages discussed above were used as the standard values for all compounds except for the larger diols (> C_{10}) previously excluded from the regression analysis and in a few cases for 1,3-propanediol. Reasons for excluding the larger α,ω-diols is discussed below.

1,3-Propanediol, which clearly shows a distinct intramolecular hydrogen bond in the gas phase, was excluded as a standard in several mixes in order to ascertain whether its vaporization enthalpy is anomalous relative to its homologues. 1,2-Ethanediol was included as a reference based on the work of Klein.[2−4] Some of the diols used in these experiments are hydroscopic. Since water is not detected by the fid, in one experiment, methanol and water (1:1) were used as solvents to determine the effect of water on retention time and peak shape. No noticeable effect was observed in peak shape or retention time, and while the results of this experiment were not included in calculating the averages, the vaporization enthalpies calculated were within the reproducibility obtained in aprotic solvents. Retention times of the all the mixtures and the results obtained in methanol/water (mix 13) are reported in the Supporting Information.

The fusion enthalpy of 1,12-dodecanediol was measured on a Perkin-Elmer DSC 7 instrument in triplicate. The instrument was calibrated using indium and validated by using naphthalene. All uncertainties provided in the tables are expressed as two standard deviations unless specified otherwise.

Results and Discussion

To determine whether the vaporization enthalpies of the α,ω-alkanediols, for which infrared spectra suggest do not form intramolecular hydrogen bonds in the gas phase, correlate with enthalpies of transfer measured by gas chromatography, 1,5-pentanediol through 1,10-decanediol were correlated as a test case. The results from this correlation are shown in Table 4, mix 1. The correlation in Table 4, characterized by a correlation coefficient of (r^2) 0.9937 and a standard deviation of ± 1.1 kJ·mol^{-1}, suggests that the enthalpies of transfer of these materials do correlate well with vaporization enthalpies and that use of the mean experimental vaporization enthalpies for these compounds is valid.

Results that include 1,2-ethanediol and 1,3-propanediol are summarized in Table 5 for three separated experiments containing α,ω-diols up to 1,7-heptanediol. The correlation equation for each respective mixture is given at the top of each section of Table 5. The average vaporization enthalpy for 1,3-propanediol, (70.9 ± 3.5) kJ·mol^{-1}, is well within the uncertainty of the average experimental vaporization enthalpy measured directly, (68.6 ± 3.2) kJ·mol^{-1} (Table 3). We conclude from the linearity observed in the α,ω-alkanediols used as standards (correlations shown in Tables 4 and 5) and the agreement found for 1,3-propanediol that use of the mean experimental vaporiza-

Table 6. Vaporization Enthalpies of 1,4-Butynediol, 2,5-Dimethyl-2,5-hexynediol, and 2,5-Dimethyl-2,5-hexanediol

mix 5	−slope	intercept	$\Delta_{sln}{}^{g}H_m(372\ K)$ J·mol^{-1}	$\Delta_l{}^{g}H_m(298.15\ K)$/J·mol^{-1} literature	calculated
$\Delta_l{}^{g}H_m(298.15\ K)/J\cdot mol^{-1} = (1.685 \pm 0.068)\Delta_{sln}{}^{g}H_m(372\ K) + (13786 \pm 885), (r^2 = 0.9968)$					
1,3-propanediol	3940.2	10.51	32757	68594	68973
1,4-butanediol	4501.4	11.251	37423	77045	76833
1,4-butynediol	4817.8	11.783	40053		81265
2,5-dimethyl-2,5-hexanediol	4968.9	11.714	41309		83381
1,6-hexanediol	5449.7	12.454	45307	91025	90115
1,7-heptanediol	5948.5	13.123	49454	96358	97101

mix 6	−slope	intercept	$\Delta_{sln}{}^{g}H_m(374\ K)$ J·mol^{-1}	$\Delta_l{}^{g}H_m(298.15\ K)$/J·mol^{-1} literature	calculated
$\Delta_l{}^{g}H_m(298.15\ K)/J\cdot mol^{-1} = (1.76 \pm 0.08)\Delta_{sln}{}^{g}H_m(372\ K) + (9990.7 \pm 469), (r^2 = 0.9979)$					
1,3-propanediol	4012	10.72	33354	68594	68767
1,4-butanediol	4550.8	11.394	37834	77045	76661
1,4-butynediol	4899.4	12.009	40732		81768
1,5-pentanediol	5002.3	11.934	41587	83069	83276

mix 7	−slope	intercept	$\Delta_{sln}{}^{g}H_m(377\ K)$ J·mol^{-1}	$\Delta_l{}^{g}H_m(298.15\ K)$/J·mol^{-1} literature	calculated
$\Delta_l{}^{g}H_m(298.15\ K)/kJ\cdot mol^{-1} = (1.7355 \pm 0.075)\Delta_{sln}{}^{g}H_m(377\ K) + (11630 \pm 904), (r^2 = 0.9963)$					
1,3-propanediol	3960.8	10.567	32929	68594	68778
2,5-dimethyl-3-hexyne-2,5-diol	4934.2	12.098	41021		82823
1,5-pentanediol	4962.2	11.815	41254	83069	83227
1,6-hexanediol	5430.5	−5429.5	45147	87844	89984
1,7-heptanediol	5920.9	13.05	49224	96358	97059

mix 8	−slope	intercept	$\Delta_{sln}{}^{g}H_m(377\ K)$ J·mol^{-1}	$\Delta_l{}^{g}H_m(298.15\ K)$/J·mol^{-1} literature	calculated
$\Delta_l{}^{g}H_m(298.15\ K)/J\cdot mol^{-1} = (1.875 \pm 0.101)\Delta_{sln}{}^{g}H_m(377\ K) + (8226 \pm 1125), (r^2 = 0.9942)$					
1,3-propanediol	3905.3	10.423	32467	68594	69089
2,5-dimethyl-3-hexyne-2,5-diol	4750.8	11.786	39496		82265
1,5-pentanediol	4776.1	11.496	39707	83069	82660
1,6-hexanediol	5244.3	12.099	43599	87844	89956
1,7-heptanediol	5718.5	12.722	47541	96358	97347

mix 9	−slope	intercept	$\Delta_{sln}{}^{g}H_m(373\ K)$ J·mol^{-1}	$\Delta_l{}^{g}H_m(298.15\ K)$/J·mol^{-1} literature	calculated
$\Delta_l{}^{g}H_m(298.15\ K)/J\cdot mol^{-1} = (2.041 \pm 0.148)\Delta_{sln}{}^{g}H_m(373\ K) - (1827 \pm 1190), (r^2 = 0.9895)$					
2,5-dimethylhexyne-2,5-diol	5016.6	14.6	41711		83295
2,5-dimethylhexane-2,5-diol	5141.5	14.459	42749		85414
1,6-hexanediol	5453.2	14.817	45341	91025	90703
1,7-heptanediol	5848.6	15.214	48628	96358	97413
1,8-octanediol	6298.6	15.768	52370	106236	105048
1,9-nonanediol	6740.6	16.33	56045	112092	112548

tion enthalpies for 1,2-ethanediol through 1,10-decanediol is also valid. Since at least, in principle, each of these diols is capable of intramolecularly hydrogen bonding in both the liquid and gas phases, we decided to examine and compare the vaporization enthalpies of some related diols that can only hydrogen bond intermolecularly. The compounds chosen for this study were 1,4-butynediol and 2,5-dimethyl-3-hexyne-2,5-diol. For comparison purposes, we have also examined the vaporization enthalpy of 2,5-dimethylhexane-2,5-diol.

1,4-Butynediol can only intermolecularly hydrogen bond in the condensed phase whereas 1,4-butanediol can intramolecularly hydrogen bond in both the liquid and the gas phases. Intramolecular hydrogen bonding should weaken intermolecular forces in the liquid phase and also stabilize 1,4-butanediol in the gas phase. Since the vaporization enthalpy measures the enthalpy difference between these two phases, intramolecular hydrogen bonding should have the effect of decreasing the vaporization enthalpy of 1,4-butanediol relative to 1,4-butynediol. The results of this study are reported in Table 6 and summarized in Table 7. The experimental results for the 1,4-butanediol/1,4-butynediol system suggests an effect of around 4 kJ·mol^{-1}. While this effect might be expected to be larger in 1,3-propanediol, which can form a six-membered ring due to intramolecular hydrogen bonding (as compared to the seven membered ring formed in 1,4-butanediol), the magnitude of the effect observed in the 1,4-butanediol/1,4-butynediol system compared with the typical magnitude of a hydrogen bond of (20 to 30 kJ·mol^{-1}) and the near linearity in vaporization enthalpy observed in Figure 2 suggest that, in the condensed phase, all α,ω-alkanediols prefer to intermolecularly hydrogen bond and that the ≈ 4 kJ·mol^{-1} effect observed is probably mostly due to the stabilization of 1,4-butanediol in the gas phase

Table 7. Comparison of the Vaporization Enthalpies of 1,4-Butynediol and 2,5-Dimethyl-2,5-hexynediol with Their Saturated Analogues

	$\Delta_l{}^{g}H_m(298.15\ K)$/J·mol^{-1} lit value	avge value, this work
1,4-butanediol	77045 ± 3600[a]	77132 ± 650
1,4-butynediol	80927[b]	81516 ± 711
2,5-dimethyl-2,5-hexanediol		85202 ± 3448
2,5-dimethyl-3-hexyne-2,5-diol		82794 ± 1030

[a] See Table 1. [b] Calculated from the Antoine constants at a mean temperature of 469 K using eq 1.[26]

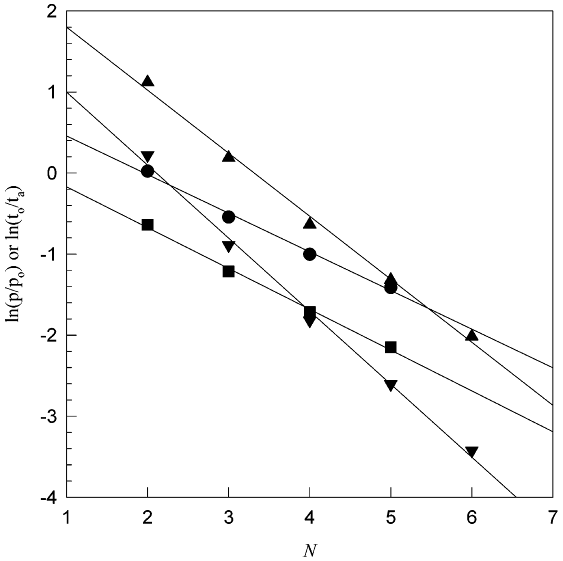

Figure 3. Circles and squares: a plot of literature $\ln(p/p_o)$ values for 1,2-ethanediol through 1,5-pentanediol at $T = (470 \text{ and } 450)$ K, respectively; triangles: a plot of $\ln(t_o/t_a)$ measured by gas chromatography against the number of carbon atoms, N, for 1,2-ethanediol through 1,6-hexanediol at $T = (340 \text{ and } 370)$ K. Values for t_o and p_o are 1 min and 101.325 kPa, respectively. Values of $\ln(p/p_o)$ were calculated from the parameters listed in Table 8, and values of $\ln(t_o/t_a)$ were calculated from the correlation equations of mix 4, Table 5.

due to intramolecular hydrogen bonding. While the strength of the intramolecular hydrogen bond in the gas phase is likely to be attenuated with an increase in ring size, an effect of this magnitude is likely to be lost in the noise associated with the experimental measurements. Consistent with this interpretation are the results obtained by comparing the vaporization enthalpies of 2,5-dimethyl-3-hexyne-2,5-diol and 2,5-dimethylhexane-2,5-diol. The vaporization enthalpies of these two compounds are within experimental error of each other. While it can be argued that steric interactions in both liquid and gas phases probably discourage intramolecular hydrogen bond formation in 2,5-dimethylhexane-2,5-diol, the hydroxyl region of the gas phase infrared spectrum of this compound is very similar to that observed for 1,4-butanediol with a sharp frequency at 3642 cm^{-1} and a broader weaker frequency 3518 cm^{-1} at 498 K.[1] According to the infrared spectrum, 2,5-dimethylhexane-2,5-diol does exhibit some intramolecular hydrogen bonding, but the effect must be small since the effect does not seem to be reflected in its vaporization enthalpy.

An additional manner of determining the effect of intramolecular hydrogen bonding in 1,3-propanediol is to compare the vapor pressure of this material relative to its homologues. Intramolecular hydrogen bonding should diminish intermolecular forces and result in an increase in volatility. It should also stabilize the diol in the gas phase. Figure 3 illustrates the effect of carbon number on experimental vapor pressure, $\ln(p/p_o)$ for 1,2-ethanediol through 1,5-pentanediol, and vapor pressure obtained indirectly by gas chromatography, $\ln(t_o/t_a)$, for 1,2-ethanediol through 1,6-hexanediol. Average values of $\ln(p/p_o)$ where $p_o = 101.325$ kPa were calculated at $T = (470 \text{ and } 450)$ K from equations in the literature; the equations used for these calculations are given in Table 8. Values of $\ln(t_o/t_a)$ were calculated from the correlation equations measured in mix 4 of Table 4 at $T = (340 \text{ and } 370)$ K. The results from both experimental vapor pressures and gas chromatographic retention times, measurement made under quite different concentrations and temperatures, show a very continuous effect of chain length on the vapor pressure of the alcohol. Changes on the extent of intra/intermolecular hydrogen bonding as a function of chain length in these diols seem to have only a small effect on relative volatility.

Table 8. Temperature Dependence of Vapor Pressure of 1,2-Ethanediol to 1,5-Pentanediol

	ΔT	$\log(p/\text{kPa}) = A - B/(T/\text{K})$		
	K	A	B	ref
1.2-ethanediol	403−470	8.3726	2994.4	10
	409−469	8.2549	2926	9
1,3-propanediol	373−488	8.2016	3018.8	11
	383−433	8.2549	3305.4	10
	433−488	8.4733	3154.9	10
1,4-butanediol	419−490	8.5149	3264	9
1,5-pentanediol	446−514	8.6049	3390	9

As noted above, α,*ω*-diols larger than C$_{10}$ were excluded from the correlation associated with eq 2. Obviously, the vaporization enthalpies of some of these compounds appear to deviate slightly from the smaller diols (Figure 2). These measurements were all reported by the research group of Piacente et al.[18,20] by mass and torsion effusion. Since the accuracy of previous measurements on hydrocarbons by these workers during this period of time have been questioned[25,27] and given the linearity observed with the smaller diols, we decided to examine the vaporization enthalpy of these materials as well by correlation gas chromatography. The results are reported in Table 9. The results of each of three correlations are given by the correlations reported at the top of each section in Table 9.

Table 10 summarizes the results of all the correlations. The values calculated by correlation gas chromatography for 1,2-ethanediol through 1,10-decanediol are all within experimental error of the average literature values reported in Table 3. Figure 4 illustrates the linearity of vaporization enthalpy as a function of number of carbon atoms, *N*, as obtained by correlation gas chromatography. The equation of the line is given by

$$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = (7.215 \pm 0.56)N + (47.876 \pm 0.81) \quad (r^2 = 0.9994) \quad (3)$$

and characterized by a standard deviation of ± 0.8 kJ·mol^{-1}.

With regards to the results on α,*ω*-diols larger than C$_{10}$, correlation gas chromatography suggests slightly larger vaporization enthalpies than those reported by Piacente et al.[18,20] However, with the exception of 1,16-hexadecanediol (and according to eq 3, 1,15-pentadecanediol), most fall within the specified uncertainties reported by these authors.

Also included in Table 10 is a summary of the vaporization enthalpies estimated using an equation developed to estimate the vaporization enthalpies of a wide class of organic compounds.[28] Applied to the diols in this study, the equation takes the form of

$$\Delta_l^g H_m(298.15\ \text{K})/\text{kJ}\cdot\text{mol}^{-1} = 4.69(N_C - N_Q) + 1.3\, N_Q + 3.0 + 2F_{OH}b_{OH} + C \quad (4)$$

where N_C and N_Q refer to the total number of carbon atoms and the number of quaternary carbons in the molecule, respectively. The symbol F_{OH} refers to the substitution factor and is based on the hybridization and substitution pattern of the carbon bearing the hydroxyl groups. The b_{OH} symbol refers to the group value of a hydroxyl group. For the α,*ω*-diols of this study, a value of 1.08 was used for F_{OH}; a value of 0.79 was used for the substitution factor in last two compounds of Table 10. The group value for a hydroxyl group is 29.4

Table 9. Vaporization Enthalpies of 1,12-Dodecanediol, 1,14-Tetradecanediol, and 1,16-Hexadecanediol

			$\Delta_{sln}^{g}H_m$(424 K)	$\Delta_l^gH_m$(298.15 K)/J·mol^{-1}	
mix 10	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_l^gH_m$(298.15 K)/J·mol^{-1} = (1.959 ± 0.147)$\Delta_{sln}^{g}H_m$(424 K) + (8165 ± 1753), (r^2 = 0.9833)					
1,6-hexanediol	5040.8	13.729	41903	91025	90271
1,7-heptanediol	5554.0	14.404	46179	96358	98648
1,8-octanediol	5907.6	14.762	49119	106236	104408
1,9-nonanediol	6395.6	15.418	53176	112092	112359
1,10-decanediol	6879.2	16.069	57197	120212	120237
1,12-dodecanediol	7826.8	17.334	65076		135675
1,14-tetradecanediol	8741.7	18.55	72683		150580
1,16-hexadecanediol	9664.9	19.793	80359		165620

			$\Delta_{sln}^{g}H_m$(428 K)	$\Delta_l^gH_m$(298.15 K)/J·mol^{-1}	
mix 11	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_l^gH_m$(298.15 K)/J·mol^{-1} = (1.814 ± 0.138)$\Delta_{sln}^{g}H_m$(428 K) + (22174 ± 1777), (r^2 = 0.9829)					
1,6-hexanediol	4521.3	12.526	37592	91025	89926
1,7-heptanediol	5103	13.38	42429	96358	98698
1,8-octanediol	5508.4	13.854	45800	106236	104812
1,9-nonanediol	6037.8	14.612	502015	112092	112795
1,10-decanediol	6495.5	15.206	54007	120212	119697
1,12-dodecanediol	7428.7	16.449	61766		133770
1,14-tetradecanediol	8330.2	17.633	69262		147365
1,16-hexadecanediol	9220.1	18.8	76661		160784

			$\Delta_{sln}^{g}H_m$(449 K)	$\Delta_l^gH_m$(298.15 K)/J·mol^{-1}	
mix 12	−slope	intercept	J·mol^{-1}	literature	calculated
$\Delta_l^gH_m$(298.15 K)/J·mol^{-1} = (2.29 ± 0.127)$\Delta_{sln}^{g}H_m$(480 K) + (5248 ± 1291), (r^2 = 0.9910)					
1,6-hexanediol	−4459.2	10.194	37072	91025	90292
1,7-heptanediol	−4870.1	10.622	40488	96358	98128
1,8-octanediol	−5234.9	10.975	43521	106236	105086
1,9-nonanediol	−5603.5	11.348	46585	112092	112115
1,10-decanediol	−6032.5	11.862	50152	120212	120297
1,12-dodecanediol	−6832.1	12.784	56799		135546
1,14-tetradecanediol	−7656.1	13.773	63650		151261

Table 10. Summary of the Vaporization Enthalpies of the α,ω-Alkanediols Studied

	$\Delta_l^gH_m$(298.15 K)/kJ·mol^{-1}			
	literature[a]	this work[b]	calcd from eq 16	calcd from eq 17
1,2-ethanediol	64.2 ± 1.2	63.9 ± 0.9	62.3 ± 1.6	68.3
1,3-propanediol	68.6 ± 3.2	69.8 ± 1.1[c]	69.5 ± 1.7	73.0
1,4-butanediol	77.0 ± 3.6	77.1 ± 0.6	76.7 ± 1.7	77.7
1,5-pentanediol	83.1 ± 7.4	83.0 ± 0.3	84.0 ± 1.7	82.4
1,6-hexanediol	91.0 ± 5.2	90.2 ± 0.3	91.2 ± 1.8	87.0
1,7-heptanediol	96.4 ± 0.3	97.9 ± 0.5	98.4 ± 1.8	99.3
1,8-octanediol	106.2 ± 1.6	104.9 ± 0.3	105.6 ± 1.9	104.0
1,9-nonanediol	112.1 ± 1.4	112.5 ± 0.2	112.8 ± 1.9	108.7
1,10-decanediol	120.2 ± 7.5	120.0 ± 0.3	120.0 ± 2.0	113.4
1,11-undecanediol	131.7 ± 4.1		127.2 ± 2.0	118.1
1,12-dodecanediol	130.5 ± 5.7	135 ± 1.2	134.5 ± 2.1	122.8
1,13-tridecanediol	132.8 ± 7.8		141.7 ± 2.2	127.5
1,14-tetradecanediol	141.7 ± 6.2	149.7 ± 2.4	148.9 ± 2.3	132.2
1,15-pentadecanediol	139.2 ± 4.4		156.1 ± 2.3	136.9
1,16-hexadecanediol	147.5 ± 4.3	163.3 ± 4.8	163.3 ± 2.4	141.5
1,4-butynediol	80.9[d]	81.5 ± 0.3		85.3
2,5-dimethylhexyne-2,5-diol		82.8 ± 0.6		80.2
2,5-dimethylhexane-2,5-diol		85.2 ± 2.6		72.6(80.2)

[a] From Table 1 unless noted otherwise. [b] Uncertainties represent two standard deviations of the mean. [c] Average of all runs (mixes 2 to 8). [d] From ref 26, adjusted to T = 298.15 K from T = 469 K using eq 1 and an estimated C_{pl} of 227.8 J·mol^{-1}·K^{-1}.

kJ·mol^{-1}. For the compounds in this study, the C term adjusts for the possibility of forming intramolecular hydrogen bonds in 5 to 9 membered rings. A value of −7.6 kJ·mol^{-1} was used for this term.[28]

Although the two equations differ significantly in slope, agreement of eq 4 with experiment is approximately within the uncertainty associated with this equation for compounds up to C_{10} (± 4 kJ·mol^{-1}). As noted previously, the error increases with larger molecules when vaporization enthalpies begin to exceed 100 kJ·mol^{-1}.[28] The value estimated for 2,5-dimethylhexyne-2,5-diol (80.2 kJ·mol^{-1}) is within experimental error of the value measured. In contrast, the value predicted for 2,5-dimethylhexane-2,5-diol is considerably less if it is assumed that it forms an intramolecular hydrogen bond as suggested by infrared studies in the gas phase. An estimated value of 80.2 kJ·mol^{-1} is predicted if it is assumed that it does not intramolecular hydrogen bond, in much better agreement with experiment.

Table 11. Sublimation Enthalpies of the α,ω-Alkanediols Studied

	$\Delta H_{cr}{}^{l}(T_{fus})$	T_{fus}	$C_p(cr)^c$	$\Delta H_{cr}{}^{l}(298\ K)^d$	$\Delta H_l{}^g(298\ K)$	$\Delta H_{cr}{}^{l}(298\ K) + \Delta H_l{}^g(298\ K)$
	kJ·mol^{-1}	K	J·mol^{-1}·K^{-1}	kJ·mol^{-1}	kJ·mol^{-1}	kJ·mol^{-1}
1,6-hexanediol	22.2 ± 1.2[a]	314.6	208.4	21.3 ± 1.2	90.2 ± 0.3	111.5 ± 1.2
1,7-heptanediol	21.3 ± 0.6[a]	295.2	235.3	21.5 ± 0.6	97.9 ± 0.5	119.4 ± 0.8
1,8-octanediol	36.1 ± 0.4[a]	332.8	262.2	33.9 ± 0.8	104.9 ± 0.3	138.8 ± 0.9
1,9-nonanediol	36.4 ± 0.4[a]	319.6	289.1	34.9 ± 0.6	112.5 ± 0.2	147.4 ± 0.6
1,10-decanediol	41.7 ± 0.6[a]	345.5	316	38.3 ± 1.2	120.0 ± 0.3	158.3 ± 1.4
1,12-dodecanediol	51.2 ± 1.3[b]	352	369.8	46.8 ± 1.9	134.5 ± 1.2	181.3 ± 2.2
1,13-tridecanediol	46.7 ± 2.8[c]	351	396.7	42.2 ± 3.1	141.7 ± 1.7[e]	183.8 ± 3.5
1,14-tetradecanediol	61.9 ± 3.7[c]	360.4	423.6	56.3 ± 4.1	149.7 ± 2.4	206.0 ± 4.8
1,15-pentadecanediol	58.7 ± 3.5[c]	361.4	450.5	52.7 ± 4.0	156.1 ± 1.9[e]	208.8 ± 4.4
1,16-hexadecanediol	64.2 ± 3.9[c]	365.4	477.4	57.6 ± 4.3	163.3 ± 4.8	220.9 ± 6.4

[a] From ref 17. [b] This work, no other transitions observed from (298.15 to 352) K, the onset temperature. [c] The sum of all enthalpy transitions above T = 298.15 K.[26] [d] Obtained by using the equation in footnote c of Table 2. [e] Obtained by using eq 4.

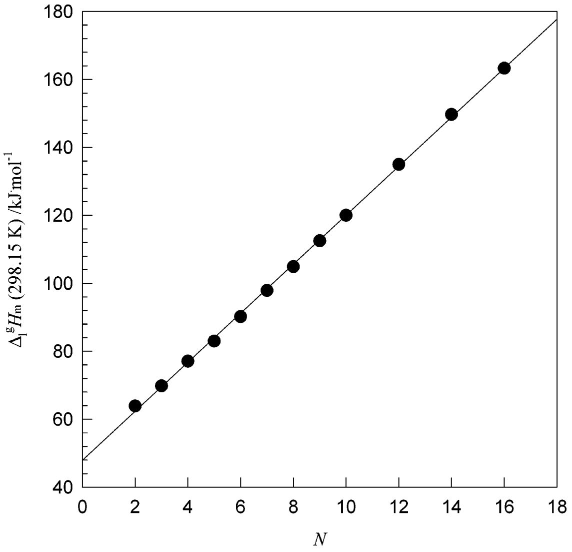

Figure 4. Vaporization enthalpies of the α,ω-alkanediols in kJ·mol^{-1} as determined by correlation gas chromatography as a function of the number of methylene groups, N, using the average vaporization enthalpy of 1,2-ethanediol through 1,10-decanediol as standards.

The presence of intramolecular hydrogen bonding as evidenced by two bands in the infrared spectrum of a compound does not necessarily have significant thermochemical consequences. In 3-buten-1-ol and 3-butyn-1-ol, the two −OH stretching bands that are observed in the infrared along with a variety of other experimental and theoretical studies have been used as evidence for the occurrence of intramolecular π−OH hydrogen bonding. Thermochemical evidence, however, has suggested that the formation of this interaction does not significantly influence the enthalpies of formation of these two molecules when the enthalpy change associated in going from the corresponding hydrocarbon to the alcohol, butane to butanol, 1-butene to 3-buten-1-ol, and 1-butyne to 3-butyn-1-ol are compared.[29]

Table 11 summarizes the sublimation enthalpies calculated by summing the vaporization enthalpies obtained by correlation gas chromatography or literature values and experimental fusion enthalpies. In cases where other solid−solid transitions occur in the diols above T = 298.15 K, these phase transitions are also included with the fusion enthalpy. Most diols above 12 carbon atoms exhibit additional solid−solid transitions.[30] Fusion enthalpies were adjusted to T = 298.15 K by using the equation in footnote c of Table 2. An uncertainty of 30 % of temperature adjustment has been included in estimating uncertainties in the fusion enthalpy at T = 298.15 K.

Conclusions

The results of the correlations obtained by gas chromatography on the α,ω-diols are generally consistent with previous literature values and suggest that the role of intramolecular hydrogen bonding in these diols has a minimal effect on the vapor pressures and vaporization enthalpies of these compounds. This is in contrast with results obtained for the corresponding α,ω-diacids. The fact that both vapor pressure and vaporization enthalpy do not appear to be sensitive indicators of intramolecular hydrogen bonding in these diols limits their usefulness in confirming the ab initio calculations of Klein with regards to the importance of intramolecular hydrogen bonding in vicinal diols.

Supporting Information Available:

Tables include retention times and a summary of each correlation. This material is available free of charge via the Internet at http://pubs.acs.org.

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