Thermochimica Acta, 232 (1994) 317–321
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01346-5

Note

Vaporization enthalpies of five odd-numbered (C_7 to C_{15}) α,ω-alkanediols

Vincenzo Piacente [a,*], Daniela Ferro [b] and Giuseppe Della Gatta [c]

[a] *Dipartimento di Chimica, Università "La Sapienza", Piazzale A. Moro 5, 00185 Rome (Italy)*
[b] *C.N.R., Centro per la Termodinamica Chimica alle Alte Temperature, c/o Dipartimento di Chimica, Università "La Sapienza", Rome (Italy)*
[c] *Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 9, 10125 Turin (Italy)*

(Received 27 April 1993; accepted 18 July 1993)

Abstract

The temperature dependence of vapour pressures for liquid C_7 to C_{15} odd-numbered terminal diols was measured by the torsion-effusion method. Corresponding vaporization enthalpies were derived.

Our continuing study of the vaporization thermodynamics of pure organic compounds [1] has included investigation on the C_6 to C_{16} homologous series of even-numbered α,ω-alkanediols [2]. This paper extends our work to the five odd-numbered (C_7 to C_{15}) members of this series.

Knauth and Sabbah [3] used a Tian–Calvet calorimeter, fitted with a Knudsen effusion cell, to measure at 323 K the vaporization enthalpies of 1,7-heptanediol and 1,9-nonanediol and a single value of their vapour pressure at the same temperature. Apart from some temperature–vapour pressure equations obtained in the high-pressure ranges and the standard vaporization enthalpies of lower diols (up to C_5) [4–7], there are apparently no other data on the odd-numbered diols in the literature.

In the present work, the temperature dependence of the vapour pressures for the C_7 to C_{15} diols were measured by the torsion-effusion method, and the corresponding vaporization enthalpies were derived.

Three diols (1,9-nonanediol (Janssen, 99%), 1,11-undecanediol (Pfaltz and Bauer) and 1,15-pentadecanediol (K & K Labs.)) were high-purity commercial products further purified by successive crystallizations from

---

* Corresponding author.

absolute ethanol (Fluka puriss., >99.8%) solutions followed by sublimation under vacuum. Because 1,13-tridecanediol is not commercially available, it was prepared by reduction of 1,11-undecanedicarboxylic acid (Pfaltz and Bauer) by $LiAlH_4$ (Aldrich, powder, 95%) in a tetrahydrofuran (Aldrich, anhydrous, 99.9%) solution. The precipitated compound was then purified through up to seven crystallizations from absolute ethanol and repeated sublimations. The purity of 1,7-heptanediol (Pfaltz and Bauer, 98%, liquid at room temperature) was improved by distillation under vacuum. Final purities were determined by the DSC peak profile method and were better than 99.8%, except for 1,7-heptanediol (about 99%). The torsion assembly was described in a previous work [8]. Two aluminium cells (effusion holes, 1.2 and 0.6 mm in diameter), were used to check the possible influence of effusion hole diameter on the pressure values, but such influence was never observed.

Table 1 reports the pressure–temperature equations obtained by least-squares treatment of the data of each run. The slope and intercepts in Table 1 were weighted according to the number of experimental points and

TABLE 1

Temperature dependence of the vapour pressure of the five odd-numbered α,ω-alkanediols measured by the torsion-effusion method

Number n of C atoms	Run	Number of points	ΔT/K	$\log(p/\mathrm{kPa}) = A - B/(T/\mathrm{K})$	
				A [a]	B [a]
7	A	14	331–360	11.79 ± 0.13	4768 ± 46
	B	21	321–360	11.80 ± 0.26	4810 ± 93
	C	14	328–360	11.44 ± 0.18	4633 ± 61
	D	13	338–361	12.62 ± 0.21	5126 ± 73
9	A	10	355–364	13.07 ± 0.73	5297 ± 264
	B	10	353–373	13.17 ± 0.44	5448 ± 161
	C	8	347–361	12.82 ± 0.48	5336 ± 171
	D	12	347–373	13.66 ± 0.39	5666 ± 142
11	A	10	355–375	15.17 ± 0.40	6356 ± 146
	B	12	357–378	16.04 ± 0.33	6687 ± 120
	C	8	360–376	15.46 ± 0.27	6502 ± 101
	D	12	357–376	15.20 ± 0.15	6390 ± 55
	E	10	352–355	14.68 ± 0.37	6161 ± 133
13	A	12	360–387	14.26 ± 0.69	6275 ± 258
	B	11	363–387	14.93 ± 0.67	6536 ± 251
	C	10	357–379	14.39 ± 0.41	6318 ± 152
15	A	9	389–399	14.54 ± 0.35	6588 ± 140
	B	10	382–400	13.86 ± 0.26	6338 ± 102
	C	9	380–401	14.46 ± 0.14	6572 ± 54

[a] The errors are standard deviations.

TABLE 2

Comparison between experimental and calculated molar vaporization enthalpies at 298 K for even- and odd-numbered C_6 to C_{16} α,ω-alkanediols

Number n of C atoms	T_{av}/ K	$\Delta_{vap}H^{\ominus}_{m}(T_{av})$/ kJ mol^{-1} [a]	$\Delta_{vap}H^{\ominus}_{m}$(298 K)/kJ mol^{-1}					
			Experimental		Calculated			
			Our work [c]	Ref. 3	Ref. 11	Ref. 12	Ref. 13	Ref. 14
6	341	87.0 ± 2.0 [b]	91 ± 3	89.8 ± 0.7 [d]	87.4	89.5	87.0	90.5
7	341	92.4 ± 1.5	97 ± 2	96.6 ± 0.6	92.4	94.5	91.7	95.6
8	356	101.1 ± 1.6 [b]	108 ± 3	103.2 ± 1.1 [d]	97.3	99.6	96.3	100.7
9	360	104.4 ± 3.4	112 ± 4	112.3 ± 1.3 [d]	102.3	104.6	101.0	105.8
10	364	112.4 ± 2.3 [b]	120 ± 3	114.1 ± 1.2 [d]	107.3	109.7	105.7	110.9
11	365	123.0 ± 1.9	131 ± 3		112.3	114.7	110.4	116.0
12	379	119.4 ± 2.7 [b]	132 ± 4		117.2	119.8	115.1	121.1
13	372	122.0 ± 3.8	132 ± 4		122.2	124.9	119.8	126.2
14	386	128.1 ± 2.9 [b]	141 ± 4		127.2	129.9	124.5	131.3
15	390	124.3 ± 1.9	138 ± 3		132.2	135.0	129.2	136.4
16	398	130.5 ± 1.8 [b]	146 ± 3		137.2	140.0	133.9	141.5

[a] The errors are standard deviations. [b] From our previous work [2]. [c] The errors are estimated. [d] Derived from $\Delta_{sub}H^{\ominus}_{m}$(298 K) and $\Delta_{fus}H^{\ominus}_{m}(T_{fus})$ also reported in ref. 3.

the following equations were derived:

for 1,7-heptanediol

$$\log(p/\text{kPa}) = 11.89 \pm 0.20 - (4826 \pm 80)(T/\text{K})$$

for 1,9-nonanediol

$$\log(p/\text{kPa}) = 13.22 \pm 0.30 - (5453 \pm 180)(T/\text{K})$$

for 1,11-undecanediol

$$\log(p/\text{kPa}) = 15.33 \pm 0.30 - (6425 \pm 100)(T/\text{K})$$

for 1,13-tridecanediol

$$\log(p/\text{kPa}) = 14.53 \pm 0.20 - (6375 \pm 200)(T/\text{K})$$

for 1,15-pentadecanediol

$$\log(p/\text{kPa}) = 14.27 \pm 0.20 - (6492 \pm 100)(T/\text{K})$$

Comparison can only be made with the vapour pressures of 1,7-heptanediol and 1,9-nonanediol measured by Knauth and Sabbah at 323 K [3]. Our average values at this temperature (8.89×10^{-4} and 2.18×10^{-4} kPa, respectively) are about twice as high as theirs (4.61×10^{-4} and 1.12×10^{-4} kPa, respectively [3]).

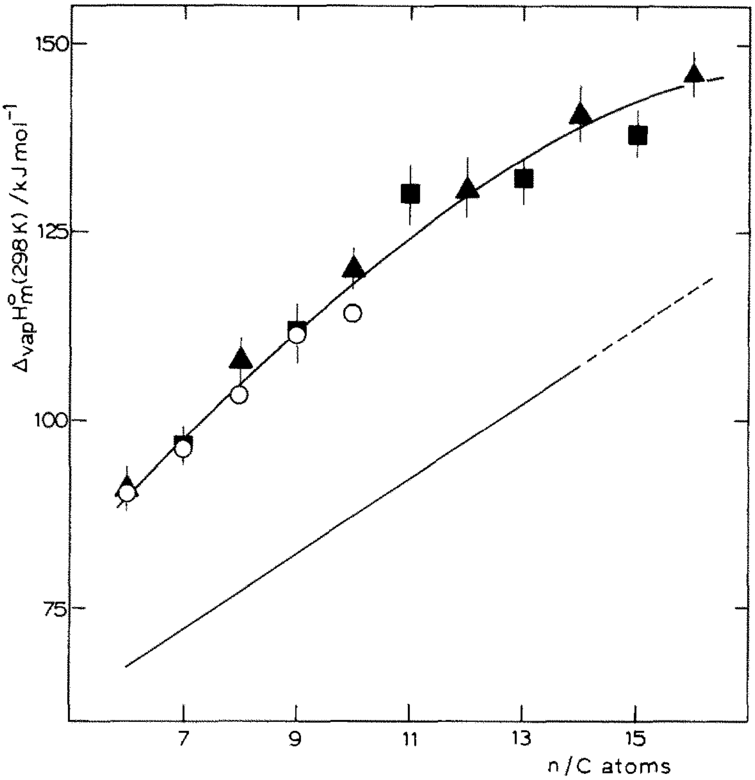

Fig. 1. Standard molar vaporization enthalpies at 298 K for even- and odd-numbered C_6 to C_{16} α,ω-alkanediols: our results (this work, ■; and ref. 2, ▲) and those from ref. 3, ○. Data for alkane-1-ols (full line) are also reported [14].

The vaporization enthalpies of our five diols at the mid-point temperatures are calculated from the slopes of the vapour–pressure equations and are reported in Table 2 (column 3). Satisfactory agreement was found with the calorimetrically measured values at 323 K for 1,7-heptanediol (93.8 ± 0.5 kJ mol^{-1}) and 1,9-nonanediol (110.0 ± 1.0 kJ mol^{-1}) [3].

As the melting points of our diols are slightly higher than 298 K, their vaporization enthalpies were converted to this temperature by considering them as undercooled liquids, except for 1,7-heptanediol, which melts at 290.5 K. The necessary enthalpy functions of the gaseous and liquid diols were obtained by using the C_p equation derived from Benson's group additivity scheme [9]

$$C_p(g) = 22.2 + 4.82n + (0.034 + 0.061n)T$$

and that proposed by Missenard [10],

$$C_p(l) = -124.6 + 18.1n + (0.712 + 0.034n)T$$

where C_p values are expressed in J mol^{-1} K^{-1} and n is the number of carbon atoms. The uncertainities of the calculated heat capacities led us to assign an error to the final vaporization enthalpies greater than that associated with the slopes of our $p-T$ equations.

The vaporization enthalpies obtained for 298 K are also reported in Table 2 (column 4) together with our previous results for the C_6 to C_{16} even-numbered diols [2], and are compared with values in ref. 3 (column 5) as well as with those estimated by different methods [11–13, 15] (columns 6–9).

A trend of $\Delta_{vap}H^{\ominus}_{m}(298\ K)$ as a function of the C atom number was found (Fig. 1). This substantially confirms the apparent decreasing contribution of the methylene group to the vaporization enthalpies already observed in ref. 2. In the present paper, accentuation of this trend is evident, since the vaporization enthalpies of 1,11-undecanediol, 1,13-tridecanediol and 1,15-pentadecanediol were practically comparable within the experimental errors.

REFERENCES

1 D. Ferro, G. Barone, G. Della Gatta and V. Piacente, J. Chem. Thermodyn., 19 (1987) 915.
G. Barone, G. Della Gatta, D. Ferro and V. Piacente, J. Chem. Soc. Faraday Trans., 86 (1990) 75.
V. Piacente, D. Ferro and G. Della Gatta, Thermochim. Acta, 158 (1990) 79.
V. Piacente and P. Scardala, Thermochim. Acta, 159 (1990) 193.
T. Pompili and V. Piacente, Thermochim. Acta, 170 (1990) 289.
2 V. Piacente, D. Ferro and G. Della Gatta, Thermochim. Acta, 223 (1993) 65.
3 P. Knauth and R. Sabbah, Can. J. Chem., 68 (1990) 731.
4 O.J. Schierholtz and M.L. Staples, J. Am. Chem. Soc., 57 (1935) 2709.
5 A.F. Gallaugher and H. Hibbert, J. Am. Chem. Soc., 59 (1937) 252.
6 P.J. Gardner and K.S. Hussain, J. Chem. Thermodyn., 4 (1972) 819.
7 P. Knauth and R. Sabbah, Bull. Soc. Chim. Fr., 5 (1988) 834.
8 V. Piacente, T. Pompili, P. Scardala and D. Ferro, J. Chem. Thermodyn., 23 (1991) 379.
9 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Haughen, H.E. O'Neal, A.S. Rodgers, R. Shaw and R. Walsh, Chem. Rev., 69 (1969) 279.
10 F.A. Missenard, Compt. Rend., 260(21) (1965) 5521.
11 M. Ducros, J.F. Gruson and H. Sannier, Thermochim. Acta, 36 (1980) 39; 44 (1981) 134.
12 J.P. Guthrie and K.F. Taylor, Can. J. Chem., 61 (1983) 602.
13 J.S. Chickos and D.G. Hesse, J. Org. Chem., 54 (1989) 5250.
14 V. Majer and V. Svoboda, in H.V. Kehiaian (Ed.), Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation, IUPAC Chemical Data Series No. 32, Blackwell Scientific Publications, Oxford, 1985.
15 E.S. Domalski and E.D. Hearing, J. Phys. Chem. Ref. Data, 22(4) (1993) 805.