

## Vaporization enthalpies of a series of $\alpha,\omega$ -alkanediols from vapour pressure measurements

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### Abstract

The standard molar vaporization enthalpies of a homologous series of six  $\alpha,\omega$ -alkanediols ( $n = 6, 8, 10, 12, 14, 16$ ) were determined from the temperature dependence of their vapour pressure measured by the torsion-effusion and Knudsen-effusion methods.

### INTRODUCTION

Alkanediols are used in several chemical fields [1–3] and as biochemical model compounds [4]. Therefore, thermodynamic information on their vaporization processes is of great interest.

Enthalpies of vaporization of low molecular weight  $\text{HO}-(\text{CH}_2)_n-\text{OH}$  ( $n = 2-6$ ) have been determined through ebullioscopic methods measuring the temperature dependence of their vapour pressure in the high pressure ranges [5–7]. Knauth and Sabbah directly measured the vaporization enthalpies of the same alkanediols ( $n = 2-5$ ) by using a Calvet microcalorimeter fitted with a vacuum effusion cell [8] and proposed the linear relation  $\Delta_{\text{vap}}H_m^\ominus(298\text{ K})/(\text{kJ mol}^{-1}) = 51.4 + 7.0n$ . In a further paper [9], these authors examined the  $n = 6-10$  range. These seem to be the only experimental data on the vaporization thermodynamics of  $\alpha,\omega$ -alkanediols reported in the literature.

In continuation of our research programme on the vaporization study of pure organic compounds [10–15], a homologous series of  $\alpha,\omega$ -alkanediols, with  $n$  ranging from 6 to 16, was studied through their vapour pressure dependence on temperature. The present paper reports results for the even-numbered diols; odd-numbered diols will be the subject of a forthcoming paper.

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## EXPERIMENTAL

The compounds investigated were commercial products from Aldrich, whose original purity ranged from 96% to 99%. They were purified by successive crystallizations from water–ethanol or absolute ethanol solution. The samples were then subjected to prolonged drying in a vacuum oven and in most cases to sublimation under vacuum.

The vapour pressures of the  $\alpha,\omega$ -alkanediols were measured by the torsion-effusion and Knudsen-effusion techniques, employing graphite cells. The method and assembly used in the torsion-effusion measurements have been described previously [15]. Vapour pressures were determined from measurements of the torsion angle ( $\alpha$ ) of the tungsten wire (30  $\mu\text{m}$  in diameter) from which the effusion cell is suspended, using the simple relation  $p = K\alpha$ , where  $K$  is a constant that takes into account the geometrical constants of the effusion cell and of the torsion wire. The value of  $K$  was determined experimentally by vaporizing standard compounds (urea, naphthalene and benzoic acid). Three cells A, B, and C with 1.2, 1.0, and 0.5 mm, respectively, effusion orifices were employed.

Furthermore, the vapour pressure of four alkanediols were also measured at lower temperatures from the mass loss rate of the sample ( $dm/dt$ ) by utilizing the well-known Knudsen equation [16]  $p = K' dm/dt(T/M)^{1/2}$ , where  $M$  is the molecular mass of the effusing vapour,  $T$  the experimental temperature and  $K'$  a constant that also takes into account the area of the effusion hole of the cell. Its value was determined as for in the torsion method.

## RESULTS AND DISCUSSION

Table 1 lists the  $\lg p$  versus  $1/T$  equations of the even-numbered  $\alpha,\omega$ -alkanediols obtained by least-squares treatment of the data measured in each torsion run. Selected equations were derived by weighing slopes and intercepts according to the number of experimental points. They are drawn in Fig. 1 and compared with those obtained from data in refs. 6 and 7. In Table 2, a general comparison of our  $p$ – $T$  equations with those of the literature is made, and some single Knudsen  $\lg p$  values from refs. 8 and 9 are also reported. Our pressure data are decidedly higher than those at only one temperature found by Knauth and Sabbah [8], which were taken above solid compounds (except for 1,9-nonanediol).

The vapour pressures of our diols with  $n = 6, 8, 10$  and  $12$  were calculated at the same temperatures as our Knudsen-effusion experiments employing the selected  $p$ – $T$  equations. The values thus obtained are compared in Table 3 with those measured; their good agreement can be taken as an indicator of the reliability of our selected equations.

Pressure values were always measured in temperature ranges in which the saturated vapour was in equilibrium with the melted samples. The

TABLE 1

Temperature dependence of the vapour pressure of  $\alpha,\omega$ -alkanediols measured by the torsion-effusion method

<i>n</i> of C atoms	Cell <sup>a</sup>	Number of points	$\Delta T/K$	$\lg(p/kPa) = A - B/(T/K)$	
				<i>A</i> <sup>b</sup>	<i>B</i> <sup>b</sup>
6	A	17	320–353	$10.91 \pm 0.35$	$4412 \pm 117$
	B	14	338–365	$11.35 \pm 0.26$	$4608 \pm 90$
	B	14	342–359	$11.47 \pm 0.31$	$4639 \pm 110$
8	A	23	340–372	$12.90 \pm 0.28$	$5272 \pm 102$
	B	13	355–372	$12.94 \pm 0.18$	$5297 \pm 64$
10	A	13	351–376	$13.89 \pm 0.44$	$5814 \pm 161$
	B	22	358–377	$14.40 \pm 0.23$	$5992 \pm 86$
	B	13	360–376	$13.71 \pm 0.38$	$5728 \pm 140$
	C	13	361–374	$14.14 \pm 0.33$	$5871 \pm 122$
12	A	15	363–395	$14.08 \pm 0.30$	$6156 \pm 115$
	B	11	369–390	$14.64 \pm 0.45$	$6350 \pm 173$
14	A	12	382–395	$14.43 \pm 0.35$	$6516 \pm 136$
	B	15	370–402	$15.06 \pm 0.58$	$6836 \pm 163$
16	A	17	376–419	$14.59 \pm 0.24$	$6789 \pm 99$
	A	15	385–405	$14.04 \pm 0.34$	$6847 \pm 135$
	B	14	402–415	$14.57 \pm 0.11$	$6783 \pm 46$
	C	14	381–418	$14.62 \pm 0.22$	$6838 \pm 90$

<sup>a</sup> See text. <sup>b</sup> The errors are standard deviations.

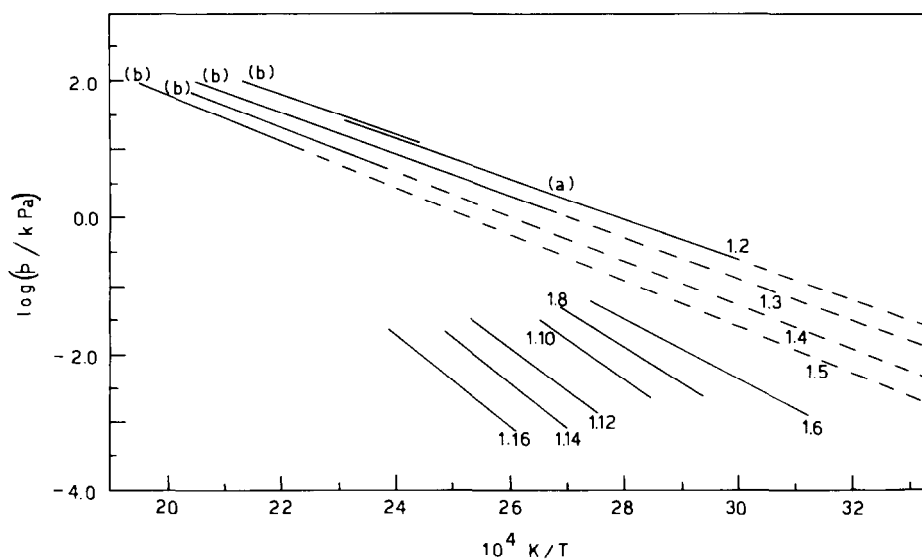


Fig. 1. Temperature dependence of the vapour pressure for liquid  $\alpha,\omega$ -alkanediols from this work and the literature data extrapolated for easier comparison (a, ref. 6; b, ref. 7).

TABLE 2

Temperature dependence of vapour pressure of  $\alpha,\omega$ -alkanediols from this work and the literature

<i>n</i> of C atoms	Ref.	Method <sup>a</sup>	$\Delta T/K$	$\lg(p/\text{kPa}) = A - B/(T/K)$	
				<i>A</i>	<i>B</i>
2	6	BP	333–443	8.329	2976.6
	5	BP	363–403	8.860	3193.6
	5	BP	403–470	8.368	2994.4
	7	BP	409–469	$8.25 \pm 0.14$	$2926 \pm 69$
	8	KE	298		–1.88
3	6	BP	373–488	8.197	3018.8
	5	BP	383–433	8.815	3305.4
	5	BP	433–488	8.468	3154.9
	8	KE	298		–2.57
4	7	BP	419–490	$8.51 \pm 0.08$	$3264 \pm 42$
	8	KE	298		–3.40
5	7	BP	446–514	$8.60 \pm 0.08$	$3390 \pm 39$
	8	KE	298		–4.40
6	7	BP	451–525	$7.60 \pm 0.16$	$3405 \pm 75$
	9	KE	298		–5.27
	This work	TE	320–365	$11.22 \pm 0.31$	$4544 \pm 106$
7	9	KE	323		–3.33
8	9	KE	323		–3.88
	This work	TE	340–372	$12.91 \pm 0.24$	$5281 \pm 88$
9	9	KE	323		–3.95
10	9	KE	342		–3.48
	This work	TE	351–377	$14.09 \pm 0.33$	$5872 \pm 121$
12	This work	TE	363–395	$14.32 \pm 0.36$	$6238 \pm 140$
14	This work	TE	370–402	$14.78 \pm 0.48$	$6694 \pm 151$
16	This work	TE	376–419	$14.45 \pm 0.23$	$6813 \pm 93$

<sup>a</sup> BP, boiling point; KE, Knudsen-effusion; TE, torsion-effusion.

molar vaporization enthalpies of the examined  $\alpha,\omega$ -alkanediols were thus determined at the mid-interval temperature ( $T_{av}$ ) from the slopes of the  $p$ – $T$  equations and are reported in Table 4, column 3.

Moreover, we have calculated their standard vaporization enthalpies at 298 K by considering them as undercooled liquids to allow comparison with other linear-chain alkyl compounds that are all liquid at this temperature. Corrections of  $\Delta_{vap}H_m^\ominus(T_{av})$  at 298 K were made by using the molar enthalpy functions derived, for the gaseous phase, from the heat capacities obtained with Benson's group additivity scheme [17]  $C_p(g) = (22.2 + 4.82n)$

TABLE 3

Vapour pressure experimental data of four  $\alpha,\omega$ -alkanediols measured by the Knudsen-effusion method

<i>n</i> of C atoms	<i>T</i> /K	Mass loss (g)	$10^{-4}\Delta t$ /s	<i>p</i> /Pa	<i>p</i> /Pa <sup>a</sup>
6	327	0.0532	6.12	2.31	2.11
	330	0.0533	5.67	2.52	2.82
	333	0.2466	16.30	4.08	3.75
8	339	0.0468	6.36	1.79	2.15
	341	0.0561	6.48	2.12	2.65
	343	0.2901	24.10	2.94	3.26
	345	0.1290	9.24	3.43	4.01
10	347	0.0481	7.20	1.51	1.47
	349	0.0552	7.14	1.75	1.84
12	359	0.0234	5.76	0.87	0.88
	361	0.1619	24.50	1.41	1.10
	362	0.0639	8.39	1.63	1.22
	362	0.0435	5.94	1.57	1.22
	364	0.0698	7.38	2.03	1.52

<sup>a</sup> Vapour pressures calculated from equations reported in Table 2.

+ $(0.034 + 0.061n)T$  (where  $n$  is the number of C atoms), and for the liquid phase those obtained with Missenard's scheme [18]  $C_p(l) = (-124.6 + 18.1n) + (0.712 + 0.034n)T$ . In Table 4 we also report the enthalpy changes for the interval  $T_{av} - 298$  K for the gaseous and liquid phases (columns 4 and 5, respectively) and the final  $\Delta_{vap}H_m^\ominus(298$  K) data (column 6). The uncertainties of the associated heat capacities led us to assign an

TABLE 4

Enthalpic data and standard molar vaporization enthalpies of  $\alpha,\omega$ -alkanediols

<i>n</i> of C atoms	$T_{av}$ /K	$\Delta_{vap}H_m^\ominus(T_{av})^a$ /kJ mol <sup>-1</sup>	$[H_m^\ominus(T_{av}) - H_m^\ominus(298$ K)] <sub>g</sub> <sup>b</sup> /kJ mol <sup>-1</sup>	$[H_m^\ominus(T_{av}) - H_m^\ominus(298$ K)] <sub>l</sub> <sup>b</sup> /kJ mol <sup>-1</sup>	$\Delta_{vap}H_m^\ominus(298$ K) <sup>c</sup> /kJ mol <sup>-1</sup>
6	342	87.0 ± 2.0	7.9	12.2	91 ± 3
8	356	101.1 ± 1.7	13.4	19.8	108 ± 3
10	364	112.4 ± 2.3	18.7	26.7	120 ± 4
12	379	119.4 ± 2.7	25.5	38.2	132 ± 4
14	386	128.1 ± 2.9	34.6	47.1	141 ± 4
16	398	130.5 ± 1.8	45.6	60.8	146 ± 3

<sup>a</sup> The errors are standard deviations. <sup>b</sup> Values obtained by using the  $C_p$  equations reported in the text.

<sup>c</sup> The errors are estimated.

TABLE 5

Comparison between experimental and calculated standard molar vaporization enthalpies of  $\alpha,\omega$ -alkanediols at 298 K

n of C atoms	Phase at 298 K	Experimental			Calculated		
		Ref. 7	Refs. 8 and 9	This work	Ref. 19	Ref. 20	Ref. 21
2	Liquid	67.8 ± 1.7	65.6 ± 0.3		67.45	69.20	68.20
3	Liquid		72.4 ± 0.3		72.43	74.26	72.89
4	Liquid	76.6 ± 1.7	79.3 ± 0.5		77.41	79.32	77.58
5	Liquid	82.4 ± 1.7	86.8 ± 0.5		82.39	84.38	82.27
6	Solid	83.3 ± 1.7	89.8 ± 0.7 <sup>a</sup>	91 ± 3	87.37	89.44	86.96
7	Liquid		96.6 ± 0.6		92.35	94.50	91.65
8	Solid		103.2 ± 1.1 <sup>a</sup>	108 ± 3	97.33	99.56	96.34
9	Solid		112.3 ± 1.3 <sup>a</sup>		102.31	104.62	101.03
10	Solid		114.1 ± 1.2 <sup>a</sup>	120 ± 4	107.29	109.68	105.72
12	Solid			132 ± 4	117.25	119.80	115.10
14	Solid			141 ± 4	127.21	129.92	124.48
16	Solid			146 ± 3	137.17	140.04	133.86

<sup>a</sup> Evaluated from the  $\Delta_{\text{sub}}H_m^\ominus(298\text{ K})$  and  $\Delta_{\text{fus}}H_m^\ominus$  values reported in ref. 9.

error to the final standard vaporization enthalpies greater than that given at  $T_{\text{av}}$  by the standard deviations of the slopes of our  $p$ - $T$  equations.

Table 5 compares our vaporization enthalpies at 298 K with the experimental values of the literature, as well as with those calculated by three bond or group additivity estimation methods [19–21]. In particular, the calorimetric  $\Delta_{\text{sub}}H_m^\ominus(298\text{ K})$  values of ref. 9 have been converted to  $\Delta_{\text{vap}}H_m^\ominus(298\text{ K})$  by using the  $\Delta_{\text{fus}}H_m^\ominus$  data reported in that paper. Our data are slightly higher than those in ref. 9, and decidedly higher than those estimated.

Figure 2 shows the  $\Delta_{\text{vap}}H_m^\ominus(298\text{ K})$  values as a function of the C atom for our  $\alpha,\omega$ -alkanediols and those from the literature compared with those of other linear homologous compounds such as alkanes [22, 23] and methylethers, alkane-1-ols, alkane-1-thiols, and  $\alpha,\omega$ -alkanedithiols [24].

All the comparison compounds display a linear dependence on the number of C atoms in the chain and a common slope of about 5 kJ per methylene, whereas diols have slightly lower [7] or higher [8, 9] slope values. Our results, initially parallel to those of ref. 9, show an apparent progressively decreasing contribution of the methylene group to the vaporization enthalpy. This could be ascribed to weakening of the intermolecular H-bonds as a consequence of a less favourable spatial configuration with increasing length of the diol molecules.

In Fig. 2, it is also worth noting that the vaporization enthalpy line for alkanols lies approximately half-way between those of the isoelectronic

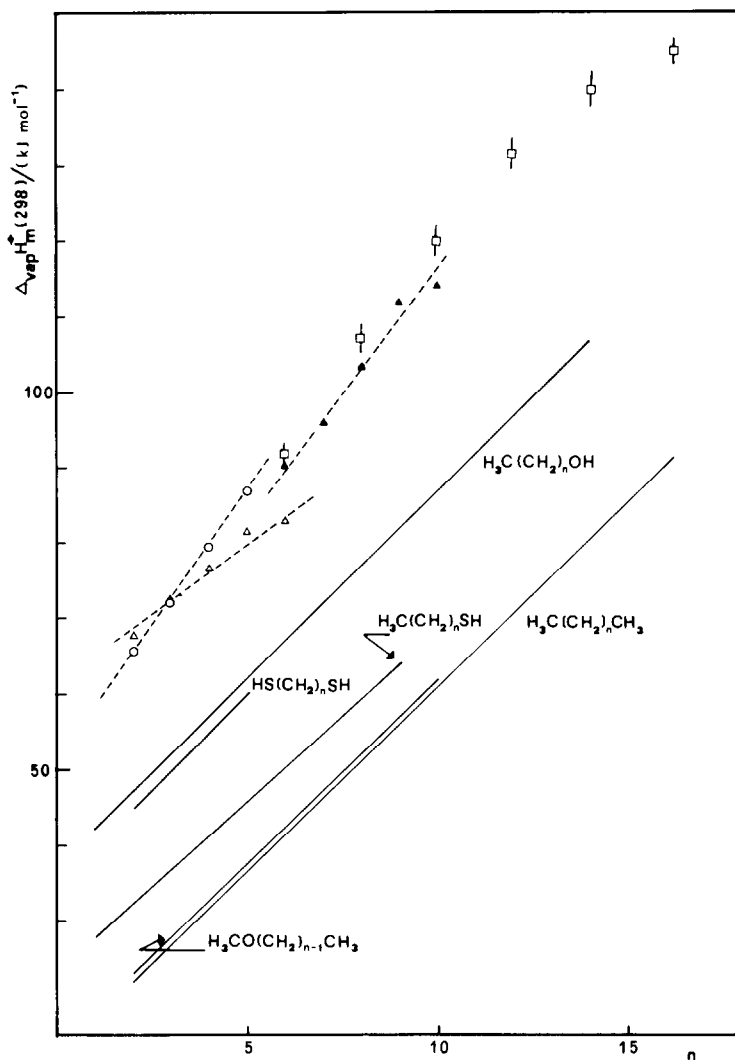


Fig. 2. Standard molar vaporization enthalpies at 298 K for  $\alpha,\omega$ -alkanediols:  $\square$ , this work;  $\triangle$ , Gardner and Hussain [7];  $\circ$  and  $\blacktriangle$ , Knauth and Sabbah [8, 9], compared with other linear homologous compounds: alkanes [22]; methylethers [24]; alkane-1-ols [24]; alkane-1-thiols [24]; and  $\alpha,\omega$ -alkanedithiols [24].

alkanes and  $\alpha,\omega$ -alkanediols, showing a clear effect of the number of hydroxyls and hydrogen bonds. In Table 6, we have calculated the contribution of the intermolecular H-bonds to the cohesive energy of liquid diols from the difference between their vaporization enthalpies and those of the isoelectronic alkanes. By ignoring the contribution of the other intermolecular interactions (about  $1 \text{ kJ mol}^{-1}$  if we compare alkanes with those of methylethers, Fig. 2), the average enthalpy value of the H-bond can be calculated to be about  $28 \text{ kJ mol}^{-1}$  by assigning two H-bonds per diol

TABLE 6

Comparison of the standard molar vaporization enthalpies  $\Delta_{\text{vap}}H_m^\ominus(298\text{ K})$  ( $\text{kJ mol}^{-1}$ ) for our  $\alpha,\omega$ -alkanediols and the isoelectronic alkanes

Compound	Number of carbon atoms $n$					
	6	8	10	12	14	16
A) $\text{HO}-(\text{CH}_2)_n-\text{OH}$	91.3	107.5	120.4	132.0	140.5	145.7
B) $\text{CH}_3-(\text{CH}_2)_n-\text{CH}_3$	41.5 <sup>a</sup>	51.4 <sup>a</sup>	61.3 <sup>b</sup>	71.1 <sup>b</sup>	81.4 <sup>b</sup>	[91.0] <sup>c</sup>
$\Delta = (\text{A}-\text{B})/2$	25	28	29	30	30	28

<sup>a</sup> Ref. 22. <sup>b</sup> Ref. 23. <sup>c</sup> Value derived from the  $\Delta_{\text{sub}}H_m^\ominus(298\text{ K}) = 152.7\text{ kJ mol}^{-1}$  [23] -  $\Delta_{\text{fus}}H_m^\ominus = 61.7\text{ kJ mol}^{-1}$  [26].

molecule (four shared bonds) [25]. This value is very close to  $26\text{ kJ mol}^{-1}$  which is the difference between the isoelectronic alkane-1-ols and alkanes, for which only one H-bond per molecule (two shared) can be assumed.

An additional interesting aspect of the data in Fig. 2 is the comparison between the vaporization enthalpies of isoelectronic dithiols and thiols, as well as of diols and alkanols, with alkanes. In particular, the (alkanedithiols-alkanes)/(alkanethiols-alkanes) and (alkanediols-alkanes)/(alkanols-alkanes) ratios are very close, 2.3 and 2.2 respectively. This may indicate that the SH functional groups are prevalently responsible for the cohesive energies in liquid mono- and bi-functional thiols, in the same way as the hydroxyl groups (and their H-bonds) are for alkane-1-ols and  $\alpha,\omega$ -alkanediols in their liquid phases.

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