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SUBLIMATION ENTHALPY OF ELEVEN ALKYL DERIVATIVES OF UREA

V. PIACENTE

Dipartimento di Chimica, Università "La Sapienza", P. le A. Moro 5, 00185 Rome (Italy)

D. FERRO

*CNR, Centro per la Termodinamica Chimica alla Alte Temperature,
c/o Dipto Chimica, Università "La Sapienza", Rome (Italy)*

G. DELLA GATTA

*Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali,
Università di Torino, via P. Guiria 9, 10125 Torino (Italy)*

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ABSTRACT

Sublimation enthalpies of eleven alkyl dervatives of urea (monomethylurea, monoethylurea, monopropylurea, monoisopropylurea, monoisobutylurea, mono-*t*-butylurea, 1,1-dimethylurea, 1,3-dimethylurea, 1,3-diethylurea, 1,3-dibutylurea and 1,1,3-trimethylurea) were determined from second-law treatment of vapour pressures measured by the torsion–effusion method and compared with earlier results.

INTRODUCTION

The sublimation enthalpies of urea and some of its derivatives, obtained from the temperature dependence of their vapour pressures, have been reported in previous papers [1,2].

Krasulin and Koziro [3] have recently used the Knudsen method to determine the vapour pressures of urea derivatives, some of which (monomethylurea (MMU), monoethylurea (MEU), monobutylurea (MBU) and 1,1-dimethylurea (1,1-DMU) had also been studied by us [1,2]. Although their absolute pressure values are comparable with ours [1], the corresponding sublimation enthalpies are generally higher, by about 5–10 kJ mol^{-1}.

The present work extends the study to other alkyl derivatives of urea (monoisopropylurea (MiPU), monoisobutylurea (MiBU), mono-*t*-butylurea (MtBU), 1,3-dibutylurea (1,3-DBU) and 1,1,3-trimethylurea (1,1,3-TrMU)) and supplies new sets of vapour pressures for those previously investigated MMU, MEU, monopropylurea (MPU), 1,1-DMU, 1,3-dimethylurea (1,3-DMU) and 1,3-diethylurea 1,3-DEU)).

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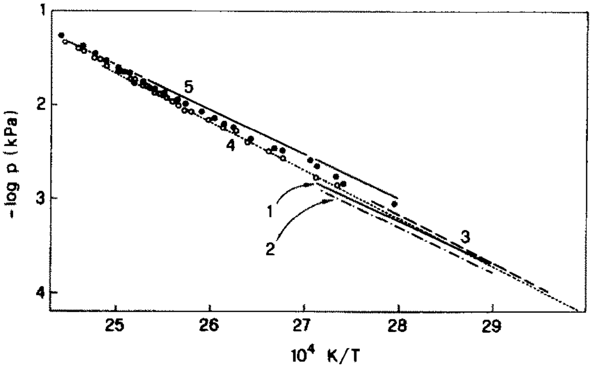

Fig. 1. Urea vapour pressures: 1 (———), ref. 9; 2 (·–·–·) ref. 10; 3 (— — —) ref. 11; 4 (······), ref. 3; 5 (———), ref. 1; ● and ○, this work.

EXPERIMENTAL

The alkyl derivatives of urea and the urea used as the reference compound were commercial products of high purity, purified by successive crystallisations from their solutions in ethyl acetate [4].

The vapour pressure of the alkyl derivatives of urea was measured by the torsion–effusion method. The assembly and method are described in previous studies [5,6]. Two conventional graphite cells with different effusion hole diameters were used. Their instrument constants, necessary for the pressure calculation, were experimentally determined by vaporising standard reference compounds (naphthalene [7] and glycerol [8]). Confirmation of the reliability of these constants was obtained by measuring the vapour pressure of urea. Our vapour pressure data are compared with those previously reported by us [1] as well as by other authors [3,9–11] (see Fig. 1).

RESULTS AND DISCUSSION

The pressure–temperature equations of the urea derivatives listed in Table 1 were obtained by least-squares treatment of the data. The experimental points are plotted in Figs. 2–4. For each derivative, a pressure–temperature equation was derived by weighting the slopes and intercepts of the equations in Table 1 in proportion to the number of data points. The equations are reported in Table 2 together with our previous results [1,2] and those determined by Krasulin and Kozyro [3] for comparison. Some vapour pressure values determined in the first vaporisation step are slightly above the log p vs. $1/T$ line obtained by taking into account all the measured pressures. As these points can be ascribed to the vaporisation of a very small amount of impurity and/or to the presence of residual crystallisation

TABLE 1

Temperature dependence of vapour pressures of alkyl derivatives of urea

Compound	Run	ΔT (K)	Number of data points	$\log p = A - B/T$	
				A [a]	B [a]
MMU	M1	344–372	18	11.30±0.17	4859±63
	M3	339–369	13	11.25±0.16	4895±60
MEU	E1	341–366	12	11.28±0.15	4860±53
	E2	345–368	12	10.93±0.22	4739±78
MPU	P1	347–386	16	11.31±0.15	4990±56
	P2	346–377	11	10.26±0.15	4524±54
	P3	346–375	10	10.42±0.13	4573±49
MiPU	iP1	370–410	22	12.20±0.16	5326±56
	iP3	368–411	16	12.17±0.11	5161±79
MiBU	iB1	354–402	19	12.35±0.14	5436±54
	iB2	353–399	18	11.59±0.15	5119±58
MtBU	tB1	359–399	18	12.17±0.11	5248±40
	tB2	361–395	13	12.56±0.10	5397±34
1,1-DMU	D1	347–372	10	11.16±0.29	4678±98
	D2	342–371	15	11.83±0.13	4938±48
1,3-DMU	3D1	334–372	14	11.12±0.10	4612±34
	3D2	336–373	16	10.77±0.10	4511±29
1,3-DEU	3E1	348–378	16	12.05±0.10	5000±30
	3E2	345–375	13	12.43±0.11	5129±40
1,3-DBU	B1	381–413	16	11.37±0.12	5250±80
	B2	379–411	16	11.62±0.12	5310±94
1,1,3-TrMU	tM1	346–374	16	11.57±0.13	4633±46
	tM2	345–375	17	11.84±0.22	4730±81

[a] The quoted errors are standard deviations.

solvent, they were not considered in the present work; this could cause the small differences observed between these and our earlier results [1].

Our absolute vapour pressures are comparable with those of Krasulin and Kozyro [3]. However, their pressure equations for MMU, MEU, MiBU and 1,1-DMU have slopes which are slightly greater than those determined in this work. Unfortunately their paper does not include experimental data so that no constructive comment can be made. The second-law sublimation enthalpies of the compounds studied were derived from the slopes of the equations obtained in this work at the middle of the experimental temperature range. Our values and those calculated by Krasulin and Kozyro are listed in Table 3, which also includes the data for MBU, not studied in the present work but reported for comparison.

Critical analysis of the error sources associated with our method (instru-

TABLE 2

Comparison of $p-T$ equations for alkyl derivatives of urea (T_{av} = average value of the experimental temperature range)

Compound	Source [ref.]	T_{av}(K)	$\log p = A - B/T$	
			A [a]	B [a]
MMU(s)	[1]	348	10.72±0.18 [b]	4562±100 [b]
	[3]	343	12.18±0.09	5196± 40
	This work	355	11.28±0.17	4874± 62
MEU(s)	[1]	346	10.20±0.18 [b]	4496±100 [b]
	[3]	343	12.35±0.03	5247± 11
	This work	354	11.11±0.19	4799± 65
MPU(s)	[1]	351	10.83±0.18 [b]	4608±100 [b]
	This work	366	10.76±0.14	4740± 53
MiPU(s) [c]	[3]	352	11.99±0.06	5212± 22
	This work	389	12.19±0.14	5257± 66
MBU(s) [d]	[2]	358	11.56±0.25	5160±100
	[3]	352	12.22±0.10	5397± 43
MiBU(s)	[3	355	12.47±0.03	5543± 26
	This work	377	11.98±0.14	5282± 56
MtBU(s)	[3]	352	12.12±0.06	5264± 18
	This work	379	12.33±0.11	5310± 37
1,1-DMU(s)	[1]	347	11.13±0.18 [b]	4655±100 [b]
	[3]	348	12.49±0.06	5180± 20
	This work	357	11.56±0.19	4834± 68
1,3-DMU(s)	[1]	344	10.78±0.18 [b]	4454±100 [b]
	This work	353	10.93±0.10	4558± 31
1,3-DEU(s) [e]	[1]	346	12.20±0.18 [b]	5047±100 [b]
	This work	361	12.22±0.10	5058± 49
1,3-DBU(l)	This work	396	11.49±0.12	5280± 87
1,1,3-TrMU(l)	This work	360	11.70±0.17	4683± 64

[a] The quoted errors are standard deviations.

[b] Estimated errors.

[c] β-MiPU phase, $\alpha \rightarrow \beta$ transition temperature 376 K [4].

[d] γ-MBU phase; $\beta \rightarrow \gamma$ transition temperature 345 K [4].

[e] β-1,3-DEU phase; $\alpha \rightarrow \beta$ transition temperature 339 K [4].

ment constants, temperature measurements, torsion angle determinations, thermodynamic equilibrium conditions in the effusion cell, etc.) suggests that the intercepts of the pressure–temperature equations may be affected by some uncertainties, those associated with the slope being decidedly

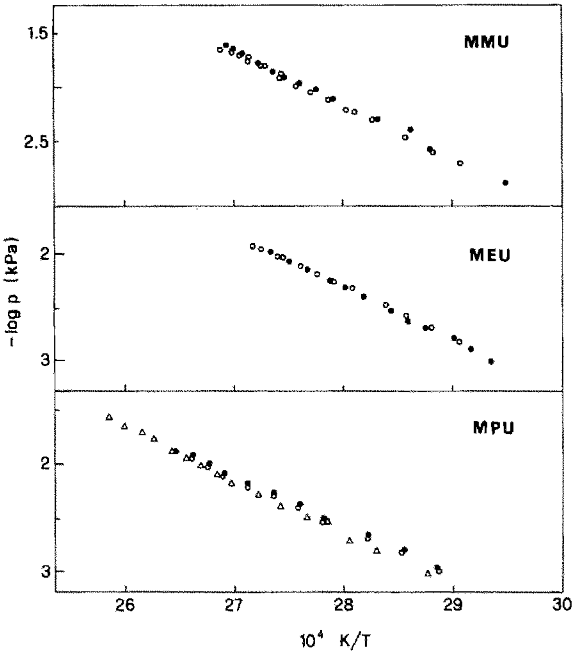

Fig. 2. Experimental vapour pressures. MMU: ●, run M3; ○, run M1. MEU: ●, run E1; ○, run E2. MPU: ●, run P2; ○, run P3; △, run P1.

TABLE 3

Sublimation enthalpies of the solid alkyl derivatives of urea

Compound	$\Delta_{\mathrm{sub}}H^{\ominus}_{T_{\mathrm{av}}}$ (kJ mol^{-1})	
	This work	Ref. 3
MMU	93.2 ± 1.1	99.3 ± 0.7
MEU	91.8 ± 1.2	100.3 ± 0.2
MPU	90.7 ± 1.0	–
MiPU [a]	100.6 ± 1.3	99.7 ± 0.4
MBU [a]	99 ± 4 [b]	103.2 ± 0.8
MiBU	101.1 ± 1.1	106.0 ± 0.5
MtBU	101.6 ± 0.7	100.7 ± 0.3
1,1-DMU	92.5 ± 1.3	99.1 ± 0.4
1,3-DMU	87.2 ± 0.6	–
1,3-DEU [a]	96.8 ± 0.9	–
1,3-DBU	116 ± 2 [c]	–
1,1,3-TrMU	104 ± 2 [d]	–

[a] See corresponding footnotes to Table 2.

[b] Estimated error reported in the original work [2].

[c] Obtained at the melting point (347 K [4]) by combining the vaporisation enthalpy (101.1 ± 1.7 kJ mol^{-1}) with the heat of fusion (15.0 kJ mol^{-1} [4]). The error is estimated.

[d] Obtained at the melting point (344 K [11]) by combining the vaporisation enthalpy (89.6 ± 1.2 kJ mol^{-1}) with the heat of fusion (14.3 kJ mol^{-1} [4]). The error is estimated.

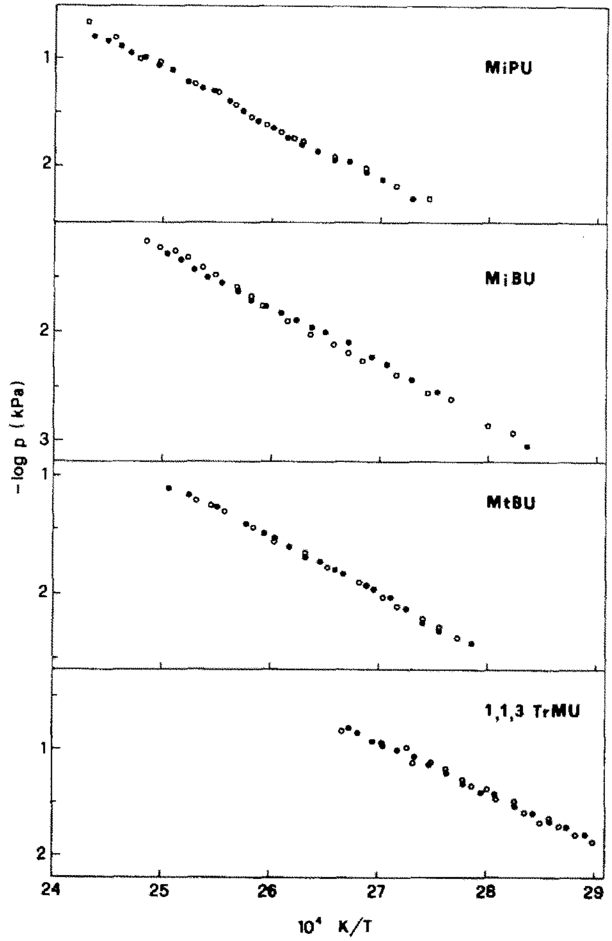

Fig. 3. Experimental vapour pressures. MiPU: ●, run iP1; ○, run iP3. MiBU: ●, run iB2; ○, run iB1. MtBU: ●, run tB2; ○, run tB1. 1,1,3TrMU: ●, run tM1; ○, run tM2.

minor. The errors associated with the second-law enthalpy values should not exceed 2–3 kJ mol^{-1}.

Table 3 shows that, except for 1,3DBU (116 ± 2 kJ mol^{-1}) and 1,1,3TrMU (104 ± 2 kJ mol^{-1}), the calculated sublimation enthalpy values of the urea derivatives studied (calculated at almost the same temperatures (350–380 K)) range from 90 kJ mol^{-1} to 100 kJ mol^{-1}.

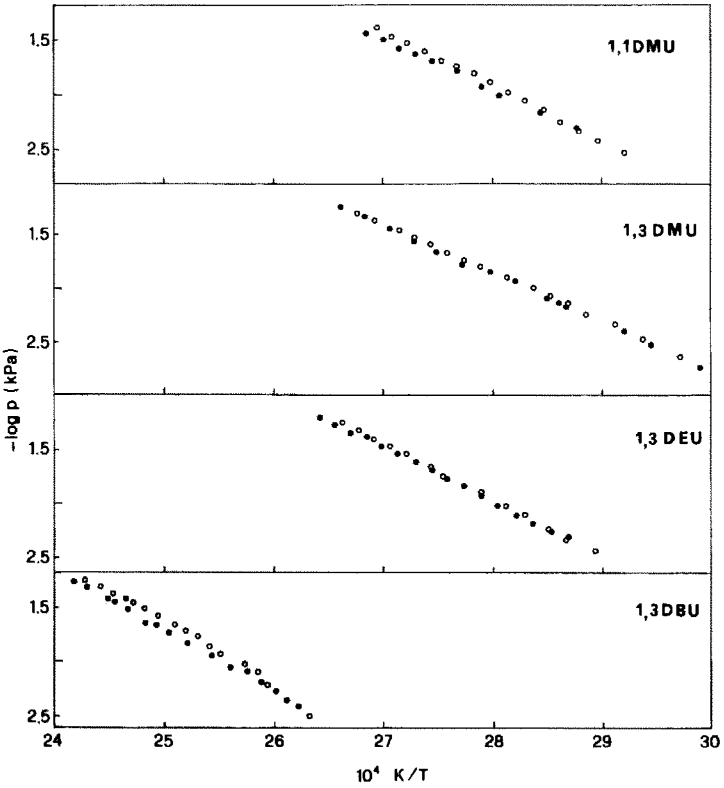

Fig. 4. Experimental vapour pressures. 1,1-DMU: ●, run D1; ○, run D2. 1,3-DMU: ●, run 3D1; ○, run 3D2. 1,3-DEU: ●, run 3E1; ○, run 3E2. 1,3-DBU: ●, run B1; ○, run B2.

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