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ENTHALPIES OF FUSION AND SOLID-TO-SOLID TRANSITION, ENTROPIES OF FUSION FOR UREA AND TWELVE ALKYLUREAS.

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SUMMARY

Enthalpies and temperatures of fusion have been measured by differential scanning calorimetry for urea and a number of its mono- and di-alkyl derivatives. Enthalpies obtained are: urea, 14.79 kJ mol^{-1}; monomethylurea, 15.75 kJ mol^{-1}; monoethylurea, 13.94 kJ mol^{-1}; monopropylurea, 14.63 kJ mol^{-1}; monoisopropylurea, 17.40 kJ mol^{-1}; monobutylurea, 14.55 kJ mol^{-1}; monotertbutylurea, 33.13 kJ mol^{-1}; dimethyl-1,1 urea, 29.61 kJ mol^{-1}; dimethyl-1,3 urea, 13.62 kJ mol^{-1}; diethyl-1,1 urea, 16.78 kJ mol^{-1}; diethyl-1,3 urea, 12.46 kJ mol^{-1}; dibutyl-1,3 urea, 14.87 kJ mol^{-1}; trimethyl-1,1,3 urea, 14.30 kJ mol^{-1}. Entropies of fusion have been derived from the experimental results.

By temperature scanning starting from r.t. some solid-to-solid transitions for four alkylureas have also been detected, all hitherto unreported. Temperatures and enthalpies of transition are: for monoisopropylurea, 375.5 K and 2.31 kJ mol^{-1}; for monobutylurea (two transitions), 313.1 K and 7.02 kJ mol^{-1}, 344.9 K and 0.88 kJ mol^{-1}; for diethyl-1,3 urea, 339.4 K and 1.87 kJ mol^{-1}; for dibutyl-1,3 urea, 311.5 K and 11.10 kJ mol^{-1}.

INTRODUCTION

Urea and its mono- and di-alkyl derivatives are of great interest in several branches of the chemical industry. Moreover, they are often employed as "model" compounds for studies in solution (refs. 1,2), particularly with respect to their influence on the structure of water solvent.

In spite of their importance, relatively few thermodynamic data on solid ureas are present in literature (ref. 3). Enthalpies of sublimation of urea and a number of its derivatives have recently been obtained by vapour-pressure measurements (ref. 4). These quantities also permit one to derive enthalpies of solvation from enthalpies of solution at infinite dilution (refs. 5-7). In this connection, a temperature scanning between r.t. and that of vapour-pressure measurements is indispensable to detect possible solid-to-solid transitions whose enthalpic balance must also be taken into account when deriving enthalpies of solvation at 298 K (ref. 8). As part of this program, we have also measured enthalpies and entropies of fusion.

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TABLE 1

List of the examined compounds, their origin and purification by crystallization from ethyl acetate solutions.

Compound	M.W.	Symbol	Origin	Comm. purity	No. crystalls.
Urea	60.06	U	Aldrich	99%	5
Monomethylurea	74.08	MMU	EGA-Chemie	99%	5
Monoethylurea	88.12	MEU	EGA-Chemie	97%	5
Monopropylurea	102.14	MPU	Kodak	n.i.	5
Monoisopropylurea	102.14	MiPU	K&K Lab.	n.i.	7
Monobutylurea	116.16	MBU	EGA-Chemie	99%	5
Monotertbutylurea	116.16	MtBU	Fluka	>97%	4
Dimethyl-1,1 urea	88.12	D(1,1)MU	Aldrich	99%	5
Dimethyl-1,3 urea	88.12	D(1,3)MU	EGA-Chemie	98%	4
Diethyl-1,1 urea	116.16	D(1,1)EU	Aldrich	99%	4
Diethyl-1,3 urea	116.16	D(1,3)EU	EGA-Chemie	97%	4
Dibutyl-1,3 urea	172.27	D(1,3)BU	K&K Lab.	n.i.	4
Trimetyl-1,1,3 urea	102.14	Tr(1,1,3)MU	Alfa Prods.	>97%	2

n.i. = not indicated by the producer

EXPERIMENTAL.

Materials.

Urea and its mono- and dialkyl derivatives were commercial high-purity grade products (97-99%) purified by several successive crystallizations from ethylacetate solutions. They are listed in Table 1 with their assigned symbols, origin, commercial purity and number of crystallizations.

Indium (5N8, Koch-Light) was used as standard of enthalpy of fusion to check sensitivity and sample temperature equations given by the supplier of the microcalorimeter (see later).

Calorimetric measurements.

The enthalpies of fusion and transition, as well as the relevant onset temperatures were measured with a Setaram DSC-111 G differential scanning calorimeter, with output recorded on a Sefram Servotrace recorder. The heating rate was in all cases 1 K min^{-1} for fusions and 3 K min^{-1} for solid-to-solid transitions, respectively.

Areas under d.s.c. peaks were measured with a Salmoiraghi mod. 237 high-precision manual planimeter, the uncertainity of this determination being evaluated as less than 0.2% for areas larger than $1x10^{3}$ mm^{2}.

The actual temperature of the sample, T_r, was obtained following the empirical equation

$$T_r/(°C) = T_p + 0.13 - 4.7x10^{-3} T_p - 0.86\ V_p \qquad (1)$$

where T_p (°C) is the temperature measured by the thermal sensor (Pt resistance) of the programmer and V_p the heating rate (°C min^{-1}).

Sensitivity,S, of the heat-flux detector was expressed by the equation

$$S/(\ \mu V\ mW^{-1}) = 6.057 + 1.483\ X\ 10^{-2}\ \bar{T}_p - 3.772x10^{-5}\ \bar{T}_p^2 + 3.934x10^{-8} \bar{T}_p^3 - 1.820x10^{-11} \bar{T}_p^4 \qquad (2)$$

where $\bar{T}_p$ (°C) is the average temperature of the examined peak, measured by the thermal sensor of the programmer.

Heat corresponding to the experimental peaks was obtained by comparing their areas with others of approximately the same magnitude whose heat was known on the basis of the sensitivity of the heat flux detector and the chart speed of the recorder.

All areas reported throughout this paper are referred to 250 μV f.s. and a chart speed of 25 mm min^{-1}. Heat-flux detector calibration equations were checked against enthalpy and temperature of fusion values of high-purity indium, and eight calorimetric runs gave $\Delta_{fus}H = (3.309 \pm 0.012)$ kJ mol^{-1} and $T_{fus} = (429.65 \pm 0.12)$ K, where uncertainities are standard deviations. By comparison with reference values (refs. 9-11), the agreement fell within the 0.5% for the enthalpy and 0.03% for the temperature.

Crimped aluminum as well as high-tightness stainless steel crucibles were used. At least one assay per compound was made under inert atmosphere by filling crucibles in a glove-box with a flux of nitrogen. For all compounds examined, we took a fresh sample for each fusion run. Samples were weighed with a Mettler microelectrobalance mod. AE 163. Four to seven runs were performed on each compound, some starting from r.t. to reveal the existence of solid-to-solid transitions, as well as possible decomposition before fusion.

TABLE 2

Experimental data for temperatures and enthalpies of fusion.

Compound	m/g	T_{fus}/K	A/mm^2	S/μVmW^{-1}	$\Delta_{fus}H$/kJ mol^{-1}
U	0.00742	406.8	5570	7.461	14.58
	0.00995	406.5	7730	7.467	14.99
	0.00828	406.8	6365	7.467	14.84
	0.01963	406.0	15120	7.467	14.87
	0.01989	406.3	15120	7.467	14.67
MMU	0.00944	373.8	6140	7.224	16.00
	0.01137	373.8	7320	7.224	15.84
	0.01131	373.8	7320	7.224	15.92
	0.00692	373.8	4290	7.224	15.26
MEU	0.00933	367.6	4370	7.169	13.81
	0.01591	367.7	7520	7.173	13.94
	0.01655	367.9	7840	7.173	13.97
	0.01538	367.9	7320	7.173	14.03
MPU	0.01360	381.1	5930	7.288	14.67
	0.02358	381.0	10430	7.288	14.81
	0.00963	381.1	4090	7.288	14.30
	0.01220	380.9	5420	7.288	14.97
	0.01270	380.9	5440	7.288	14.42
MiPU	0.00497	427.5	2640	7.595	17.16
	0.00956	426.7	5140	7.590	17.36
	0.00474	427.8	2600	7.596	17.71
	0.00510	427.7	2665	7.594	16.88
	0.00758	427.6	4100	7.596	17.45
	0.00631	427.4	3450	7.595	17.64
	0.00993	427.3	5400	7.579	17.59
MBU	0.01280	369.3	4900	7.182	14.88
	0.01080	369.2	4050	7.182	14.55
	0.01040	369.4	3895	7.182	14.55
	0.02604	369.4	9800	7.182	14.61
	0.01480	369.1	5590	7.186	14.65
	0.01890	369.4	6995	7.182	14.36
	0.02122	369.2	7790	7.182	14.26
MtBU	0.01221	449.3	10535	7.697	31.21
	0.01072	450.6	10110	7.714	34.02
	0.00709	449.9	6880	7.711	35.06
	0.01077	449.4	9600	7.709	32.25

TABLE 2

continued

Compound	m/g	T_{fus}/K	A/mm^2	S/μV mW^{-1}	$\Delta_{fus}H$/kJ mol^{-1}
D(1,1)MU	0.01216	453.2	13185	7.725	29.70
	0.00964	454.1	10380	7.723	29.49
	0.00994	453.9	10760	7.723	29.65
	0.01069	454.3	11535	7.732	29.51
	0.01252	453.9	13590	7.732	29.70
	0.01433	454.3	15560	7.732	29.70
	0.01260	454.0	13600	7.732	29.54
D(1,3)MU	0.01670	379.3	7620	7.264	13.28
	0.01650	379.6	7620	7.264	13.43
	0.01494	379.8	7030	7.272	13.69
	0.01039	379.3	4930	7.272	13.80
	0.01359	379.3	6490	7.272	13.89
D(1,1)EU	0.02210	342.5	9100	6.931	16.56
	0.02090	342.2	8775	6.936	16.87
	0.01830	342.2	7630	6.931	16.77
	0.00959	342.3	4040	6.931	16.94
D(1,3)EU	0.02306	383.7	7490	7.303	12.40
	0.01839	383.5	5940	7.303	12.33
	0.01464	383.6	4800	7.303	12.52
	0.01147	383.0	3675	7.296	12.24
	0.01039	383.4	3480	7.303	12.79
	0.01550	383.0	5130	7.303	12.64
	0.02306	383.7	7445	7.303	12.32
D(1,3)BU	0.01005	346.9	2530	6.981	14.91
	0.01347	347.0	3400	6.981	14.95
	0.01226	347.0	3490	6.981	14.64
	0.01082	346.8	2705	6.981	14.81
	0.01084	346.8	2710	6.981	14.81
	0.01538	347.1	3887	6.981	14.97
	0.01455	347.0	3700	6.981	15.02
Tr(1,1,3)MU	0.02237	344.6	9075	6.956	14.29
	0.02459	344.4	9950	6.956	14.26
	0.02311	342.9	9300	6.956	14.18
	0.03196	345.3	13130	6.961	14.47
	0.02574	345.0	10460	6.966	14.30

RESULTS

Experimental data concerning fusions and solid-to-solid transitions are reported in Tables 2 and 3, respectively. Column 1 gives the amount of compound in g, column 2 the onset temperature of the fusion/transition peak in K, column 3 the area, A, of the peak in mm^2, column 4 the sensitivity, S, of the heat-flux detector in μVmW^{-1}, and column 5 the fusion/transition enthalpy in kJ mol^{-1}.

Urea. Five calorimetric runs led to $\Delta_{fus}H$ = (14.79 ± 0.16) kJ mol^{-1} and a temperature of fusion of (406.5 ± 0.3) K, where uncertainities are standard deviations. It is known that urea gradually decomposes during melting, so that enthalpy of fusion regularly decreases in successive melting-solidification runs (ref. 12). In our experiments, this effect was avoided by using a fresh sample for each measurement. No small endothermic effects were observed before melting by contrast with what was observed by Bros et al. (ref. 12) and Khattab et al. (ref. 13), although at quite different temperatures, 360 and 387 K respectively. Literature values in kJ mol^{-1} for the enthalpy of fusion of urea are: 14.51 (ref. 14), 13.47 ± 0.25 (ref. 3), 13.61 (ref. 20), 14.41 (ref. 12), 35.5 (?) (ref. 13), 15.52 (ref. 15).

Monomethylurea. Four calorimetric runs led to $\Delta_{fus}H$ = (15.75 ± 0.33) kJ mol^{-1} and a temperature of fusion of (373.8 ± 0.03) K.

Monoethylurea. Four calorimetric runs led to $\Delta_{fus}H$ = (13.94 ± 0.09) kJ mol^{-1} and a temperature of fusion of (367.8 ± 0.1) K. Literature value: (13.97 ± ± 0.17) kJ mol^{-1} (ref. 3).

Monopropylurea. Five calorimetric runs led to a value of (14.63 ± 0.27) kJ mol^{-1} for the enthalpy of fusion, and a temperature of (381.0 ± 0.1) K.

Monoisopropylurea. Our d.s.c. measurements (six runs) showed a fully reversible solid-to-solid transition at (375.5 ± 0.6) K with $\Delta_{trs}H$ = (2.31 ± 0.05) kJ mol^{-1}. Seven calorimetric runs led to $\Delta_{fus}H$ = (17.40 ± 0.29) kJ mol^{-1} and to T_{fus} = (427.4 ± 0.4) K.

Monobutylurea. Two solid-to-solid transitions were revealed by d.s.c. runs. The $\alpha \rightarrow \beta$ transition occurs at (313.1 ± 0.7) K with an endothermic effect of (7.02 ± ± 0.14) kJ mol^{-1}, values being obtained from seven calorimetric runs. The α-phase is recovered from the β one only by freezing under 250 K. By contrast, the $\beta \rightarrow \gamma$ transition (eight runs) appears to be fully reversible and occurs at (344.9 ± 0.1) K with an endothermic effect of (0.88 ± 0.05) kJ mol^{-1}. Seven fusion runs gave $\Delta_{fus}H$ = (14.55 ± 0.20) kJ mol^{-1} and T_{fus} = (369.3 ± 0.1) K.

Monotertbutylurea. Four calorimetric runs led to $\Delta_{fus}H$ = (33.13 ± 1.73) kJ mol^{-1} and T_{fus} = (449.8 ± 0.6) K. The uncertainity on enthalpy of fusion value is higher than for other ureas, in relation to possible decomposition during melting (ref. 16).

Dimethyl-1,1 urea. Seven calorimetric runs led to $\Delta_{fus}H$ = (29.11 ± 0.09) kJ mol^{-1} and T_{fus} = (454.0 ± 0.4) K. Literature value: (22.97 ± 0.25) kJ mol^{-1} (ref. 3).

Dimethyl-1,3 urea. Five calorimetric runs gave a value of (13.62 ± 0.25) kJ mol^{-1} for the enthalpy of fusion, and a T_{fus} = (379.5 ± 0.2) K. Literature values are (12.43 ± 0.25) kJ mol^{-1} (ref. 3) and (12.9 ± 1.4) kJ mol^{-1} (ref. 17).

TABLE 3

Experimental data for temperatures and enthalpies of transition.

Compound	m/g	T_{trs}/K	A/mm^2	S/μVmW^{-1}	$\Delta_{trs}H$/kJ mol^{-1}
MiPU	0.00956	376.0	650	7.280	2.29
	0.00474	375.7	325	7.272	2.31
	0.00510	374.4	338	7.256	2.24
	0.00758	375.7	514	7.272	2.28
	0.00631	375.7	450	7.272	2.40
	0.00510	375.7	350	7.272	2.32
MBU	0.01280	314.1	2175	6.672	7.10 (1st)
		344.8	300	6.991	0.94 (2nd)
	0.02604	313.4	4300	6.672	6.90 (1st)
		345.0	575	6.991	0.88 (2nd)
	0.02978	344.8	625	6.991	0.84 (2nd)
	0.06081	344.8	1350	6.991	0.89 (2nd)
	0.04287	313.4	7050	6.672	6.87 (1st)
	0.03578	313.3	5975	6.672	6.98 (1st)
		344.8	800	6.991	0.89 (2nd)
	0.02120	312.7	3500	6.672	6.90 (1st)
	0.02800	312.5	4850	6.672	7.24 (1st)
		344.8	550	6.991	0.78 (2nd)
	0.03673	344.8	825	6.991	0.90 (2nd)
	0.01480	312.0	2525	6.672	7.13 (1st)
		345.1	325	6.991	0.88 (2nd)
D(1,3)EU	0.01464	340.7	725	6.966	1.98
	0.01147	336.8	575	6.922	2.02
	0.03206	339.2	1410	6.972	1.76
	0.03374	338.9	1530	6.978	1.81
	(2nd cycle)	341.2	1520	6.971	1.80
D(1,3)BU	0.01005	311.3	1750	6.632	10.86
	0.01347	311.6	2375	6.632	10.99
	0.01226	311.6	2215	6.632	11.25
	0.00742	311.3	1300	6.649	10.90
	0.01084	311.5	1950	6.632	11.21
	0.01538	311.7	2750	6.602	11.20
	0.01455	311.8	2625	6.602	11.30

TABLE 4

Enthalpies and temperatures of solid-to-solid transition and fusion, entropies of fusion for urea and alkylureas.

Compound	N	T_{trs}/K	$\Delta_{trs}H$/kJ mol^{-1}	N	T_{fus}/K	$\Delta_{fus}H$/kJ mol^{-1}	$\Delta_{fus}S$/J K^{-1} mol^{-1}
U		-	-	5	406.5(0.3)	14.79(0.16)	36.4(0.4)
MMU		-	-	4	373.8(0.0)	15.75(0.33)	42.1(0.9)
MEU		-	-	4	367.8(0.1)	13.94(0.09)	37.9(0.2)
MPU		-	-	5	381.0(0.1)	14.63(0.27)	38.4(0.7)
MiPU	6	375.5(0.6)	2.31(0.05)	7	427.4(0.4)	17.40(0.29)	40.7(0.7)
MBU	7	313.1(0.7)	7.02(0.14)				
	8	344.9(0.1)	0.88(0.05)	7	369.3(0.1)	14.55(0.20)	39.4(0.5)
MtBU		-	-	4	449.8(0.6)	33.13(1.73)	73.6(3.8)
MPhU*		-	-		420.0(0.1)	23.68(0.31)	56.3(0.7)
D(1,1)MU		-	-	7	454.0(0.4)	29.61(0.09)	65.2(0.2)
D(1,3)MU		-	-	5	379.5(0.2)	13.62(0.25)	35.9(0.6)
D(1,1)EU		-	-	4	342.3(0.1)	16.78(0.16)	49.0(0.5)
D(1,3)EU	4	339.4(1.7)	1.87(0.12)	7	383.4(0.3)	12.46(0.20)	32.5(0.5)
D(1,3)BU	7	311.5(0.2)	11.10(0.18)	7	346.9(0.1)	14.87(0.13)	42.8(0.3)
D(1,3)PhU*		-	-		512.1(1.9)	34.62(1.38)	66.5(1.7)
Tr(1,1,3)MU		-	-	5	344.4(0.9)	14.30(0.10)	41.5(0.3)

In brackets: standard deviations.

N = No. of calorimetric runs.

*Mono- and di-phenylurea: data from ref. 18.

Diethyl-1,1 urea. Four calorimetric runs led to $\Delta_{fus}H$ = (16.78 ± 0.16) kJ mol^{-1} and a temperature of fusion of (342.3 ± 0.1) K.

Diethyl-1,3 urea. Our calorimetric measurements (four runs) showed a reversible solid-to-solid transition ($\alpha \rightarrow \beta$) occurring at (339.4 ± 1.7) K accompanied by an endothermic effect of (1.87 ± 0.12) kJ mol^{-1}. Seven calorimetric runs led to $\Delta_{fus}H$ = (12.46 ± 0.20) kJ mol^{-1} and T_{fus} = (383.4 ± 0.3) K.

Dibutyl-1,3 urea. Seven calorimetric runs revealed a reversible solid-to-solid transition ($\alpha \rightarrow \beta$) at (311.5 ± 0.2) K showing an endothermic effect of (11.10 ± 0.18) kJ mol^{-1}. The same samples gave also: $\Delta_{fus}H$ = (14.87 ± 0.13) kJ mol^{-1} and T_{fus} = (346.9 ± 0.1) K.

Trimethyl-1,1,3 urea. Five calorimetric runs led to Δ_{fus} = (14.30 ± 0.10) kJ mol^{-1} and a temperature of fusion of (344.4 ± 0.9) K.

Average values of enthalpies and temperatures of fusion and transition with their standard deviations are reported for all samples in Table 4, in which results concerning monophenylurea and diphenyl-1,3 urea (ref. 18) are also reported for comparison. Values of entropy can be considered in rough agreement with Walden's rule, which suggests that the enthalpy of fusion divided by melting point is equal to ca. 55 J K^{-1} mol^{-1} for non-associated substances (ref. 19). Only the result concerning monotertbutylurea appears unusually high (73.6 J K^{-1} mol^{-1}), thus confirming the presence during melting of interfering thermal effects probably due to initial decomposition (ref. 16).

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