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# **Enthalpies and Entropies of Sublimation of Some Primary Alkylamides**

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The vapor pressures of some primary alkylamides, as later on reported, were measured by a torsioneffusion method in rather extended intervals of temperature. The following pressure-temperature equations were selected: propanamide,  $\log(p/\text{kPa}) = (10.6 \pm 0.4) - (3940 \pm 200) \text{ K}/T$ ,  $\Delta T = (283-343)$ K; butanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K}$ ; hexanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K}$ ; hexanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K}$ ; hexanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K}$ ; hexanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K}$ ; hexanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K}$ ; hexanamide,  $\log(p/k\text{Pa}) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/T}$ ,  $\Delta T = (298-347) \text{ K/T}$ . kPa) =  $(11.0 \pm 0.4) - (4430 \pm 200)$  K/T,  $\Delta T = (301-371)$  K; octadecanamide,  $\log(p/\text{kPa}) = (16.2 \pm 0.4)$ - (7370  $\pm$  200) K/T,  $\Delta T =$  (384-459) K; 2-methylpropanamide,  $\log(p/k\text{Pa}) = (11.2 \pm 0.3) - (4300 \pm 200)$ K/T,  $\Delta T = (288-354)$  K; 2,2-dimethylpropanamide,  $\log(p/kPa) = (12.2 \pm 0.3) - (4640 \pm 100)$  K/T,  $\Delta T =$ (298-359) K. From these equations the second-law enthalpies and entropies of sublimation were derived. Because the average value of all of the experimental temperature ranges were sufficiently near room temperature, the obtained thermodynamic data were assumed as standard. The vaporization of octadecanamide was studied above the molten compound so that the vaporization data was opportunely corrected for the fusion data: propanamide,  $\Delta_{\text{sub}}H^{2}(298 \text{ K}) = (75 \pm 4) \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{sub}}S^{2}(298 \text{ K}) = (164 \pm 4) \text{ kJ}$ 8) J mol<sup>-1</sup> K<sup>-1</sup>; butanamide,  $\Delta_{\text{sub}}\dot{H}^{\text{e}}(298 \text{ K}) = (82 \pm 4) \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{sub}}\mathcal{S}^{\text{e}}(298 \text{ K}) = (174 \pm 8) \text{ J mol}^{-1} \text{ K}^{-1}$ ; hexanamide,  $\Delta_{\text{sub}} H^{\circ}(298 \text{ K}) = (85 \pm 4) \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{sub}} S^{\circ}(298 \text{ K}) = (172 \pm 8) \text{ J mol}^{-1} \text{ K}^{-1}$ ; octadecanamide,  $\Delta_{\text{sub}}H^{\text{P}}(298 \text{ K}) = (196 \pm 4) \text{ kJ mol}^{-1}, \Delta_{\text{sub}}S^{\text{C}}(298 \text{ K}) = (418 \pm 8) \text{ J mol}^{-1} \text{ K}^{-1}; 2\text{-methylpropanamide}, \Delta_{\text{sub}}H^{\text{P}}-100 \text{ cm}^{-1} \text{ kJ}^{-1}$  $(298 \text{ K}) = (82 \pm 4) \text{ kJ mol}^{-1}, \Delta_{\text{sub}} \mathcal{S}'(298 \text{ K}) = (179 \pm 6) \text{ J mol}^{-1} \text{ K}^{-1}; 2,2\text{-dimethylpropanamide}, \Delta_{\text{sub}} \mathcal{H}^{-1}$  $(298 \text{ K}) = (89 \pm 2) \text{ kJ mol}^{-1}, \Delta_{\text{Sub}} S(298 \text{ K}) = (195 \pm 6) \text{ J mol}^{-1} \text{ K}^{-1}$ . Comparisons with the literature data are reported.

#### Introduction

The knowledge of thermodynamic data associated with the phase transitions and in particular with the sublimation process for organic compounds is fundamental in the study of their structure and stability. Moreover, these quantities are useful in many thermodynamic calculations, ranging from thermochemistry to solution chemistry, biochemistry, and biophysics. As part of our ongoing program on the vaporization study of organic compounds, the sublimation enthalpies of the following alkylamides were determined by measuring their vapor pressures: propanamide (Pa), butanamide (Ba), hexanamide (Hexa), octadecanamide (Octa), 2-methylpropanamide (2-mPa), and 2,2-dimethylpropanamide (2,2-dmPa). Thermodynamic data concerning the sublimation of some of the straightchain alkylamides studied in the present work were determined previously by Davies et al. and reported in one of a series of their papers (Davies et al., 1959). Dynamic tensimetric values for Pa and Ba at high temperatures were given by Thomas (1960). Some vapor pressure values for 2-mPa and 2,2-dmPa were measured by Abbaud et al. (1989) using the Knudsen method. Apparently no other thermodynamic data concerning the sublimation of the compounds studied have been found in the literature.

#### **Experimental and Results**

The primary alkylamides used in this study were

commercial products from Aldrich (Pa, 97%; 2-mPa, 99%; Hexa, 98%; 2,2-dmPa, 98%) and Fluka (Ba, >98%; Octa,  $\sim$ 90%). The compounds, except 2-mPa which was used as received, were purified by repeated crystallization from ethanol solutions, dried under vacuum at room temperature, and kept in a desiccator until their use. The purity of all samples was checked by the DSC peak-profile method and was always better than about 99.7%.

The vapor pressures of the compounds were measured by using two torsion-effusion assemblies, A and B, described in two previous works (Piacente et al., 1991, 1994, respectively). The assemblies are substantially different for the heating systems and for the length of their torsion tungsten wires. To extend the experimental temperature range, two thermostatic baths were used for heating the assembly A, a Thermal H5S (from Julabo Labortechnik GMBH) for the measurements at low temperature (between 280 and about 340 K) and a mineral oil for higher temperatures. In both assemblies the sample temperature was measured with an uncertainty of about ±0.2 K and the torsion angles lower than about 5° were determined with an error of about 10% (for higher angles the errors in their measurements were negligible). Three conventional graphite cells, C1, C2, and C3, with different areas of their effusion holes  $(7.1 \times 10^{-2}, 1.77, \text{ and } 3.1 \text{ mm}^2,$ respectively) were employed. The instrumental constants of these cells were determined by vaporizing two very pure standard compounds having well-known vapor pressures, benzoic acid (Colomina et al., 1982) and cadmium (Hultgreen et al., 1973). Several checks showed a reproducibility of about 5% for the instrument con-

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			Propa					
run 1 (cell C <sub>2</sub> , assembly A)		A)	run 2 (cell C <sub>1</sub>	, assembly A)	ru	run 3 (cell C <sub>1</sub> , assembly B)		
<i>T</i> /K	-log( <i>p</i> /l	(Pa)	<i>T</i> /K	-log(p/kPa)			-log(p/kPa)	
283	3.34		307	2.15	302		2.39	
285	3.26		311	1.99	311		1.99	
286	3.14		317	1.74	313		1.91	
289	3.04		321	1.59	316		1.79	
291	2.93		326	1.43	319		1.67	
294	2.81		329	1.27	322		1.51	
298	2.63		333	1.12	327		1.35	
301 302	2.52 2.50		338 343	0.95	331 335		1.20 1.05	
302	2.30 2.42		343	0.83	340		0.89	
306	2.30				340		0.03	
			Butar	amide				
un 1 (cell (	C <sub>2</sub> , assembly A)	run 2 (cel	l C <sub>2</sub> , assembly B)		1, assembly A)	run 4 (cel	l C <sub>1</sub> , assembly E	
<i>T</i> /K	-log(p/kPa)	<i>T</i> /K	-log(p/kPa)	<i>T</i> /K	$-\log(p/\text{kPa})$	<i>T</i> /K	-log(p/kPa	
298	3.14	300	3.18	311	2.69	325	2.09	
302	2.96	302	3.07	316	2.39	329	1.91	
306	2.79	305	2.94	320	2.29	332	1.81	
309	2.68	309	2.79	326	2.09	335	1.69	
313	2.50	312	2.64	332	1.81	339	1.50	
314	2.45	315	2.52	336	1.63	344	1.31	
317	2.33	317 321	2.44 2.26	340 345	1.45 1.26	347	1.20	
		321			1.20			
run 1 (cell C <sub>2</sub> , assembly A) run 2 (		run 2 (cel	l C <sub>2</sub> , assembly B)	namide	1, assembly A)	run 4 (cell C <sub>1</sub> , assembly		
T/K	$\frac{-\log(p/\text{kPa})}{-\log(p/\text{kPa})}$		$\frac{-\log(p/\text{kPa})}{-\log(p/\text{kPa})}$	<i>T</i> /K	$\frac{1, \operatorname{dissembly}(A)}{-\log(p/kPa)}$	<i>T</i> /K	-log(p/kPa	
301	3.74	305	3.56	318	2.84	330	2.39	
308	3.44	306	3.52	322	2.69	335	2.15	
317	3.00	309	3.34	327	2.51	339	2.09	
321	2.84	311	3.26	332	2.39	344	1.91	
326	2.59	315	3.09	337	2.15	347	1.79	
330	2.45	317	3.00	342	1.95	352	1.58	
335	2.23	320	2.84	348	1.71	356	1.39	
340 345	2.02 1.87	325 329	2.74 2.50	352 357	1.58 1.35	361 365	1.25 1.11	
343	1.07	332	2.37	361	1.21	303	1.11	
		336	2.21	366	1.04			
		341	2.05	371	0.88			
			Octadeo	anamide				
		-	l C <sub>3</sub> , assembly A)	run 3 (cell C <sub>1</sub> , assembly B)		run 4 (cell C <sub>2</sub> , assembly		
<i>T</i> /K	-log(p/kPa)	T/K	-log(p/kPa)	<i>T</i> /K	-log(p/kPa)	7/K	-log(p/kPa	
413	1.64	407	$1.94 \\ 1.64$	390 396	2.60	384 388	2.96	
419 425	1.46 1.24	412 418	1.64	396 401	2.33 2.12	388 393	2.74 2.49	
423 431	0.99	422	1.29	404	1.94	397	2.49	
437	0.74	429	0.96	410	1.70	401	2.08	
441	0.54	435	0.70	414	1.53	405	1.91	
449	0.25	441	0.48	419	1.32	409	1.76	
454	0.04	447	0.29	423	1.19	412	1.61	
459	-0.10	452	0.09			416	1.45	
						420 426	1.28	
			Q Madlard	ononomida		426	1.05	
un 1 (cell (	C <sub>1</sub> , assembly A)	run 9 (cal	2-Metnyipi l C <sub>1</sub> , assembly B)	run 3 (cell C	<sub>2</sub> , assembly A)	run 4 (cel	l C <sub>2</sub> , assembly I	
T/K	$\frac{-\log(p/\text{kPa})}{-\log(p/\text{kPa})}$	7/K	$\frac{-\log(p/\text{kPa})}{-\log(p/\text{kPa})}$	7/K	$\frac{-\log(p/kPa)}{-\log(p/kPa)}$	7/K	-log(p/kPa	
310	2.51	312	2.47	288	3.64	290	3.49	
315	2.29	316	2.26	295	3.24	296	3.18	
317	2.21	320	2.09	299	2.99	299	3.05	
321	2.04	326	1.84	302	2.90	302	2.87	
325	1.88	332	1.61	307	2.69	306	2.69	
330	1.69	336	1.43	312	2.46	311	2.51	
334	1.54	340	1.33			314	2.40	
338 342	1.36	345 350	1.13			319	2.16	
342 347	1.13 1.00	350	0.97			324 329	1.95 1.75	

2,2-Dimethylpropanamide										
run 1 (cell C <sub>2</sub> , assembly A)		run 2 (cell C <sub>2</sub> , assembly B)		run 3 (ce	ll C <sub>3</sub> , assembly A)	run 4 (cell C <sub>1</sub> , assembly B)				
<i>T</i> /K	-log(p/kPa)	<i>T</i> /K	-log(p/kPa)	<i>T</i> /K	$T/K$ $-\log(p/kPa)$		-log(p/kPa)			
298	3.34	299	3.34	326	2.09	325	2.15			
301	3.26	302	3.14	330	1.88	329	1.91			
304	3.09	305	3.04	334	1.67	333	1.69			
307	2.96	310	2.74	340	1.46	336	1.63			
310	2.81	312	2.61	345	1.28	341	1.45			
313	2.63	316	2.46	349	1.12	344	1.33			
316	2.51	319	2.33	353	0.96	347	1.20			
319	2.37	322	2.20	356	0.84	350	1.10			
323	2.23	327	2.00	359	0.77					
327	2.04									
328	1.93									
329	1.86									

Table 2. Temperature Dependence of the Vapor Pressures of the Studied Alkylamides

					$\log(p/kPa) = A - B/(T/K)$		
compound	run	cell (assembly)	no. of points	$\Delta T/K$	A	В	
propanamide	1	C <sub>2</sub> (A)	11	283-306	$10.07 \pm 0.29$	$3790 \pm 84$	
•	2	C <sub>1</sub> (A)	9	307 - 343	$10.74 \pm 0.24$	$3957 \pm 76$	
	3	C <sub>1</sub> (B)	10	302 - 340	$11.12\pm0.12$	$4078 \pm 39$	
butanamide	1	C <sub>2</sub> (A)	7	298 - 317	$10.34\pm0.17$	$4019 \pm 51$	
	2	C <sub>2</sub> (B)	8	300 - 321	$10.62\pm0.17$	$4138 \pm 53$	
	3	C <sub>1</sub> (A)	8	311 - 345	$11.52\pm0.43$	$4416\pm141$	
	4	$C_1$ (B)	7	325 - 347	$12.04\pm0.24$	$4594 \pm 79$	
hexanamide	1	$C_2(A)$	9	301 - 345	$11.17 \pm 0.14$	$4493 \pm 46$	
	2	C <sub>2</sub> (B)	12	305 - 341	$10.77 \pm 0.24$	$4367 \pm 76$	
	3	$C_1(A)$	12	318 - 371	$11.13\pm0.24$	$4462 \pm 82$	
	4	$C_1$ (B)	9	330 - 365	$10.98 \pm 0.41$	$4418\pm142$	
octadecanamide	1	C <sub>3</sub> (A)	9	413 - 459	$16.36\pm0.37$	$7462 \pm 160$	
	2	C <sub>3</sub> (A)	9	407 - 452	$16.32\pm0.30$	$7416\pm129$	
	3	C <sub>1</sub> (B)	8	390 - 423	$15.70\pm0.23$	$7135 \pm 92$	
	4	C <sub>2</sub> (B)	11	384 - 426	$16.42\pm0.19$	$7431 \pm 75$	
2-methylpropanamide	1	C <sub>1</sub> (A)	11	310 - 354	$11.58 \pm 0.23$	$4372\pm75$	
	2	C <sub>1</sub> (B)	9	312 - 350	$11.28\pm0.16$	$4281 \pm 51$	
	3	C <sub>2</sub> (A)	6	288 - 312	$11.51 \pm 0.60$	$4354 \pm 180$	
	4	$C_2$ (B)	10	290 - 329	$11.05\pm0.17$	$4214 \pm 52$	
2,2-dimethylpropanamide	1	$C_2(A)$	12	298 - 329	$12.28\pm0.30$	$4671 \pm 94$	
V	2	C <sub>2</sub> (B)	9	299 - 327	$12.33\pm0.35$	$4678 \pm 110$	
	3	$C_3(A)$	9	326 - 359	$12.17\pm0.24$	$4636 \pm 82$	
	4	$C_1$ (B)	8	325 - 350	$11.97\pm0.52$	$4572\pm174$	

stants, and this corresponds to a displacement of about  $\pm 0.02$  in the logarithm of pressure values. The secondlaw sublimation enthalpies of the calibrating compounds, evaluated from the slope of the logarithm of the torsion angles vs 1/T equations, were found to be in very good agreement with those selected in the literature, and this shows that equilibrium conditions were attained in the cells.

The vapor pressure data of Pa, Ba, Hexa, Octa, 2-mPa, and 2,2-dmPa are reported in Table 1. The results are summarized in Table 2 as  $\log p$  vs 1/T equations derived by linear least-squares treatment of the experimental data of each run. The errors associated with the slopes and intercepts of these equations are standard deviations. The slight inconsistencies among the  $\log p$  vs 1/T equations reported in Table 2 could be due both to the casual errors in the experimental data of each run and to expectable failure of the least-squares treatment of the data when applied to a small number of points. Apparently no evident dependence of the pressure values on the area of the effusion holes was observed. For each compound giving a weight to the slope and intercept of each pressure equation proportionally to the number of the experimental points, the following final equations of the studied alkylamides were selected:

propanamide

$$log(p/kPa) = (10.6 \pm 0.4) - (3940 \pm 200) \text{ K/}T$$
  
 $\Delta T = (283-343) \text{ K} (1)$ 

butanamide

$$log(p/kPa) = (11.1 \pm 0.4) - (4290 \pm 200) \text{ K/}T$$
  
 $\Delta T = (298-347) \text{ K} (2)$ 

hexanamide

$$log(p/kPa) = (11.0 \pm 0.4) - (4430 \pm 200) \text{ K/}T$$
  
 $\Delta T = (301-371) \text{ K} (3)$ 

octadecanamide

$$log(p/kPa) = (16.2 \pm 0.4) - (7370 \pm 200) \text{ K/}T$$
  
 $\Delta T = (384-459) \text{ K} (4)$ 

2-methylpropanamide

$$log(p/kPa) = (11.2 \pm 0.3) - (4300 \pm 200) \text{ K/}T$$
  
 $\Delta T = (288-354) \text{ K} (5)$ 

2,2-dimethylpropanamide

$$log(p/kPa) = (12.2 \pm 0.3) - (4640 \pm 100) \text{ K/}T$$
  
 $\Delta T = (298-359) \text{ K} (6)$ 

The associated errors were estimated. These equations are reported in Table 3 and given in Figures 1-6 for comparison with those found in the literature.

Table 3. Comparison with the Literature of the Vapor Pressures and Standard Sublimation Thermodynamic Data of the Studied Alkylamides

			no. of		$\log(p/kPa) = A - B/(T/K)$		$\Delta_{\text{sub}}H^{\circ}(298 \text{ K})/$	$\Delta_{\text{sub}} S^{\circ}(298 \text{ K})/$
compound	ref	method	points	$\Delta T/K$	A	В	(kJ mol <sup>-1</sup> )	$(J \text{ mol}^{-1} \text{ K}^{-1})$
propanamide(s)	Davies et al. (1959)	transpiration	8	318-346	11.2	4139	$79.2 \pm 0.3$	$175\pm0.8$
propanamide(l)	Thomas (1960)	dynamic	11	381 - 493	$8.4\pm0.1$ a	$3155\pm22^a$	$73.3 \pm 0.5$ <sup>b</sup>	$160\pm2^{b}$
propanamide(s)	this work	torsion	30	283 - 343	$10.6\pm0.4$	$3940 \pm 200$	$75\pm4$	$164\pm 8$
butanamide(s)	Davies et al. (1959)	transpiration	11	336 - 382	11.7	4513	$86.4 \pm 0.5$	$186\pm1$
butanamide(s)	Davies et al. (1959)	Knudsen	4	298 - 341	11.9	4546	$87.0 \pm 0.8$	$189\pm2$
butanamide(l)	Thomas (1960)	dynamic	10	398 - 504	$8.3\pm0.1$ a	$3176\pm24^a$	$79.9 \pm 0.6$ <sup>c</sup>	$169\pm1^{c}$
butanamide(s)	this work	torsion	30	298 - 347	$11.1\pm0.4$	$4290\pm200$	$82\pm4$	$174 \pm 8$
hexanamide(s)	Davies et al. (1959)	transpiration	8	338 - 368	12.4	4967	$95.1 \pm 0.4$	$200\pm1$
hexanamide(s)	this work	torsion	42	301 - 371	$11.0\pm0.4$	$4430\pm200$	$85\pm4$	$172\pm 8$
octadecanamide(s)	Davies et al. (1959)	Knudsen	6	367 - 379	23.6	10230	$196\pm1$	$412\pm3$
octadecanamide(s)	Davies et al. (1959)	Knudsen	6	367 - 379	23.8	10224	$196 \pm 4$	$418\pm 8$
octadecanamide(l)	this work	torsion	37	384 - 459	$16.2\pm0.4$	$7370\pm200$	$196\pm4^d$	$418\pm 8^d$
2-methylpropanamide(s)	Abbaud et al. (1989)	Knudsen	6	286 - 302	$11.83 \pm 0.04$	$4497.9\pm10.9$	$86.1 \pm 0.2$	$188.0 \pm 0.8$
2-methylpropanamide(s)	this work	torsion	36	288 - 354	$11.2\pm0.3$	$4300\pm200$	$82\pm4$	$179 \pm 6$
2,2-dimethylpropanamide(s)	Abbaud et al. (1989)	Knudsen	7	288 - 306	$11.77 \pm 0.06$	$4522.9\pm20.0$	$86.6 \pm 0.4$	$186.9\pm1$
2,2-dimethylpropanamide(s)	this work	torsion	38	298 - 359	$12.2\pm0.3$	$4640\pm100$	$89\pm2$	$195\pm 6$

 $^a$  Calculated by us employing the experimental data report in the paper. (The errors are the standard deviations.)  $^b$  Obtained using the fusion data:  $T_{\rm fus}=(352.6\pm0.1)$  K,  $\Delta_{\rm fus}H^{\rm e}=(12.9\pm0.1)$  kJ mol $^{-1}$ , Della Gatta et al. (2000).  $^c$  Obtained using the fusion data:  $T_{\rm fus}$ =  $(387.3 \pm 0.1)$  K,  $\Delta_{\text{fus}}\dot{H}^{\text{p}} = (19.2 \pm 0.2)$  kJ mol<sup>-1</sup>, Della Gatta et al. (2000). d Obtained using the fusion data:  $T_{\text{fus}} = (380.0 \pm 0.2)$  K,  $\Delta_{\text{fus}}H^{\circ} = (55.3 \pm 0.4) \text{ kJ mol}^{-1}, \text{ Della Gatta et al. (2000)}.$ 

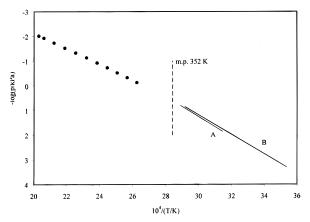


Figure 1. Torsion vapor pressure of propanamide: A, Davies et al. (1959); B, this work; ●, Thomas (1969).

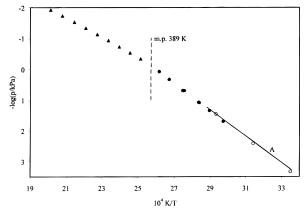


Figure 2. Torsion vapor pressure of butanamide: O, Davies et al. (1959) (Knudsen data); ●, Davies et al. (1959) (transpiration data); A, Thomas (1969); A, this work.

#### **Discussion**

In this paper the vapor pressures of some amides were measured by a torsion method over a fairly large temperature range. From the slopes and intercepts of the selected linear  $\log p$  vs 1/T equations, the second-law sublimation enthalpy and entropy were derived and reported in Table 3. These thermodynamic data, to which were associated decidedly overestimated errors, were considered standard

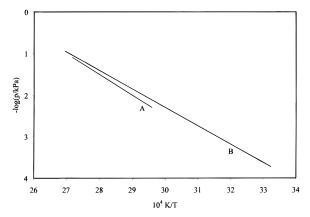


Figure 3. Torsion vapor pressure of hexanamide: A, Davies et al. (1959); B, this work.

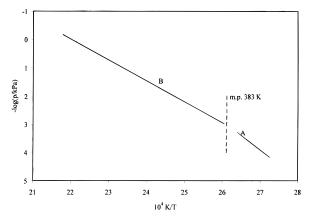
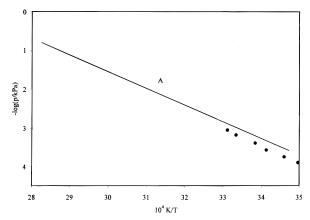


Figure 4. Torsion vapor pressure of octadecanamide: A, Davies et al. (1959); B, this work.

because all of the midpoints of the covered experimental temperature ranges are near room temperature. Because the vapor pressure for Octa was measured above the molten compound, to obtain the sublimation thermodynamic data, the vaporization values were corrected by using the fusion data ( $T_{\text{fus}} = 380 \text{ K}$ ,  $\Delta_{\text{fus}} H = 55.3 \text{ kJ mol}^{-1}$ ) calorimetrically determined by Della Gatta et al. (2000). A detailed comparison of our data with those found in the literature is presented in Table 3 and in Figures 1-6. Both our sublimation entropy and enthalpy of Pa and Ba are in



**Figure 5.** Torsion vapor pressure of 2-methylpropanamide: ●, Abbaud, (1989); A, this work.

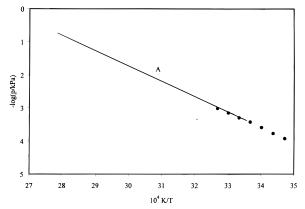


Figure 6. Torsion vapor pressure of 2,2-dimethylpropanamide: •, Abbaud, (1989); A, this work.

agreement with the literature data, as well as those measured at high temperatures, reported at 298 K only by the fusion data. Good agreement was found also for the data obtained above both molten compounds by Thomas and for Octa. The sublimation thermodynamic data, even though the absolute vapor pressure values for Hexa are comparable (see Figure 3), are in poor agreement. Concerning 2-mPa and 2,2-dmPa, the vapor pressures measured by Abbaud et al. (1989) above both compounds are practically equal so that the derived sublimation thermodynamic data are also equal. On the contrary, the vapor pressure measured in the present work shows different temperature dependencies. Considering the wider experimental temperature ranges and the higher number of pressure values,

we believe that our results can be considered more reliable. An interesting comparison can be made in our data for Pa (monomethylacetamide), 2-mPa (dimethylacetamide), and 2,2-dmPa (trimethylacetamide). Their vapor pressures were measured in a comparable temperature range, and their sublimation enthalpies and entropies show linear trends, (75  $\pm$  4), (82  $\pm$  2), and (89  $\pm$  2) kJ mol<sup>-1</sup> for the enthalpy values of mono-, di-, and trimethylacetamide, respectively (with an increment of about 7 kJ mol<sup>-1</sup> (-CH<sub>3</sub> group) $^{-1}$ ) and (164  $\pm$  10), (179  $\pm$  6), and (195  $\pm$  6) J mol $^{-1}$  $K^{-1}$  for the sublimation entropies for mono-, di-, and trimethylacetamide, respectively (with the increment of about 15 J mol<sup>-1</sup> K<sup>-1</sup> (-CH<sub>3</sub> group)<sup>-1</sup>). Moreover, even though the number of our compounds is decidedly small, the results of the present work lead one to doubt that the increment of the sublimation enthalpy per carbon atom, corresponding to the contribution of the solid -CH<sub>2</sub>group, can be assumed to be that proposed by Davies (4.3 kJ mol<sup>-1</sup> for  $C_2$ ,  $C_4$ , and  $C_6$ , 7.2 kJ mol<sup>-1</sup> for  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$ , and  $C_{18}$ , and 5.0 kJ mol<sup>-1</sup> for  $C_3$ ,  $C_5$ , and  $C_7$ ). Of course, it will be necessary to study a further group of alkylamides to better point out the possible trends of the sublimation thermodynamic parameters in their homologous series.

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