J. Chem. Eng. Data **2008,** *53,* 959–965

Heat Capacities and Enthalpies of Solid−Solid Transitions and Fusion of a Series of Eleven Primary Alkylamides by Differential Scanning Calorimetry

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Molar heat capacities at constant pressure, $C_{p,\mathrm{m}}$, of 11 primary alkylamides (butanamide, 2-methylpropanamide, pentanamide, 2,2-dimethylpropanamide, hexanamide, octanamide, decanamide, dodecanamide, hexadecanamide, octadecanamide, docosanamide) determined by differential scanning calorimetry (DSC) increased as a function of temperature and were fitted into linear equations. Values at 298.15 K obtained by interpolating/extrapolating the smoothed equations displayed a linear increase with the number of carbon atoms. The $C_{p,\mathrm{m}}$ contribution of the CH_2 group was (22.5 ± 0.7) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, in agreement with our previous results for linear alkane-α,ω-diamides and alkane-α,ω-diols as well as with the literature data for various series of linear alkyl compounds. Temperatures, enthalpies, and entropies of the solid−solid transitions and fusion of alkylamides were also determined. They are discussed with reference to the packing patterns described in the literature.

Introduction

Precise evaluation of the molar heat capacity, $C_{p,\mathrm{m}}$, as a function of temperature is fundamental for deriving the enthalpy and entropy of sublimation at 298.15 K and the enthalpy of solvation as well as the partial molar heat capacities of solution at infinite dilution.[1–6] In addition, knowledge of the changes in thermodynamic quantities during phase transitions is of great importance in the study of the structure and stability of organic compounds.[7–10] This paper provides an overall picture of the solid phase thermodynamic behavior of 11 primary alkylamides, namely, their molar heat capacities and their solid−solid and solid−liquid phase transitions. $C_{p,\mathrm{m}}$ was measured in the temperature range T = (183 to 323) K or, in some cases, in narrower temperature ranges in compliance with the solid−solid transitions of alkylamides. The contribution of the CH_2 group to heat capacity in this series was also determined and compared with other values for series of alkyl compounds studied by some of us or found in the literature.

The thermodynamic properties of solid alkylamides have received little attention in the literature, except for acetamide[11,12] (phase transitions and heat capacity), octadecanamide[13,14] (phase transitions), and 2-methylpropanamide and 2,2-dimethylpropanamide (heat capacities).[15] Their thermodynamic properties of fusion and solid−solid transition and heat capacities are mostly unknown. Vapor pressure dependence on temperature and sublimation thermodynamic parameters, however, have been reported in the literature[15,16] and investigated by some of us.[17]

Primary alkylamides (hereinafter alkylamides) are simple organic compounds characterized by a balance among hydrogen bonding, dipole–dipole interactions, and dispersive forces typical of the ubiquitous interactions within peptides and proteins. Correlations may be established between their fusion thermodynamic properties and intermolecular forces and crystal packing arrangements.

Experimental Section

Materials. The 11 alkylamides examined in this work are listed in Table 1, with their formula, CAS registry number, adopted symbol, molar mass M, commercial origin, temperature of fusion T_{fus}, and mass fraction w. All compounds were purified by successive crystallizations from absolute ethanol (Fluka puriss.) and dried to constant mass under reduced pressure at room temperature. The final mass fraction was always better than 0.99, as determined by the DSC peak profile method.[19]

High-purity indium (SRM 758) from NIST, naphthalene (CRM No. M16-03) from NPL, gallium (mass fraction 0.99999), hexane (GC standard, mass fraction ≥ 0.997), and octane (mass fraction ≥0.998) from Fluka, and water (mass fraction 0.99999) from Aldrich were used as reference materials for temperature and enthalpy calibration. Benzoic acid (CRM No. M16-06) from NPL was used as reference material for heat flow calibration.[20] Urea (SRM 2152) from NIST was used as an internal standard for heat capacity measurements.

Phase Transition Temperature and Enthalpy Measurement. The enthalpies of solid−solid transitions and fusion and the corresponding onset temperatures were measured in Turin with a Setaram DSC 111 and in Catania with a Mettler DSC 30, at a heating rate of 16.7 $\mathrm{mK{\cdot}s^{-1}}$.

For the measurements with Setaram DSC 111, the actual temperature of phase transition T of the samples was obtained by using the empirical equation supplied by the manufacturer

$$T/\mathrm{K} = T_{\mathrm{p}} + 0.13 - 4.7\cdot10^{-3}(T_{\mathrm{p}} - 298.15) - 51.6V_{\mathrm{p}}/\mathrm{K}\cdot\mathrm{s}^{-1} \qquad (1)$$

where T_{p} is the temperature measured by the thermal sensor (a Pt resistance) of the programmer of the calorimeter and V_{p} is the selected heating rate. This equation was obtained by the

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10.1021/je700662a CCC: $40.75

Table 1. Primary Alkylamides with Their CAS Registry Number, Formula, Adopted Symbol, Molar Mass M, Commercial Origin, Temperature of Fusion T_{fus}, and Mass Fraction w

compound[a]	CAS registry no.	formula	symbol	M^b (g·mol^{-1})	origin	T_{fus} K[c]	$w^{c,d}$
propanamide (propionamide)	79-05-0	$CH_3-CH_2-CONH_2$	C_3	73.094	Lancaster	353 to 356	0.99
butanamide (butyramide)	541-35-5	$CH_3(CH_2)_2-CONH_2$	C_4	87.121	Fluka	387 to 389	>0.98
2-methylpropanamide (isobutyramide)	563-83-7	$(CH_3)_2(CH)-CONH_2$	i-C_4	87.121	Aldrich	400 to 402	0.99
pentanamide (valeramide)	626-97-1	$CH_3(CH_2)_3-CONH_2$	C_5	101.148	TCI	378	>0.98
2,2-dimethylpropanamide (pivalamide)	754-10-9	$(CH_3)_3(C)-CONH_2$	t-C_5	101.148	Aldrich	427 to 430	0.98
hexanamide (caproamide)	628-02-4	$CH_3(CH_2)_4-CONH_2$	C_6	115.175	Aldrich	373 to 375	0.98
octanamide (caprylamide)	629-01-6	$CH_3(CH_2)_6-CONH_2$	C_8	143.228	TCI	378	>0.98
decanamide (capramide)	2319-29-1	$CH_3(CH_2)_8-CONH_2$	C_{10}	171.282	TCI	371	>0.97
dodecanamide (lauramide)	1120-16-7	$CH_3(CH_2)_{10}-CONH_2$	C_{12}	199.336	TCI	372	0.99
hexadecanamide (palmitamide)	629-54-9	$CH_3(CH_2)_{14}-CONH_2$	C_{16}	255.443	TCI	379	0.97
octadecanamide (stearamide)	124-26-5	$CH_3(CH_2)_{16}-CONH_2$	C_{18}	283.496	Fluka	377 to 380	>0.90
docosanamide (behenamide)	3061-75-4	$CH_3(CH_2)_{20}-CONH_2$	C_{22}	339.604	TCI	377	>0.80

[a] In brackets, the common names of compounds from NIST Chemistry WebBook. [b] Based on the 1999 IUPAC Table of Standard Atomic Weights of the Elements and its 2001 revision.[18] [c] Values given by the manufacturer. [d] After purification, mass fraction ranged from 0.990 to 0.999.

Table 2. Comparison between Temperatures of Fusion T_{fus} and Molar Enthalpies of Fusion $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ Measured with our DSC Apparatuses and Literature Values for the Selected Reference Materials[a]

			T_{fus}/K		$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/(kJ·mol^{-1})	
compound	origin	N^b	this work	literature	this work	literature
indium	NIST	4	429.40 ± 0.08^c	429.748 ± 0.00034^e	3.266 ± 0.05^c	3.273 ± 0.022^e
gallium	Fluka	4	303.72 ± 0.08^c	302.9146^e	5.57 ± 0.12^c	5.583 ± 0.009^e
naphthalene	NPL	4	353.27 ± 0.04^d	353.39 ± 0.03^f	18.94 ± 0.003^d	19.05 ± 0.04^f
octane	Fluka	4	216.35 ± 0.06^d	216.38^g	20.69 ± 0.07^d	20.74^g

[a] Uncertainties are expressed as twice the standard deviation of the mean. [b] Number of calorimetric runs. [c] Setaram DSC 111. [d] Mettler DSC 30. [e] Ref 20. [f] Certificate of Measurement CRM No. M16-03. [g] Ref 21.

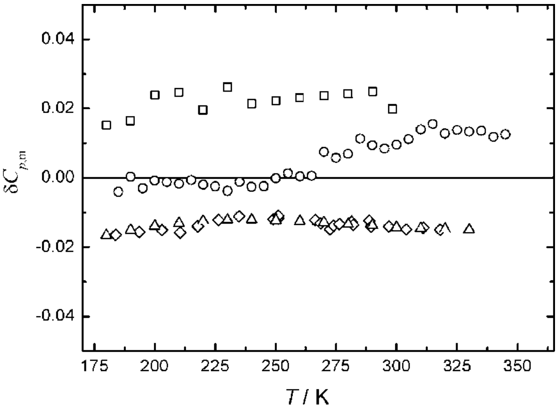

Figure 1. Molar heat capacity of urea as a function of temperature: deviations of literature values from our data $\delta C_{p,\mathrm{m}} = [C_{p,\mathrm{m}}$ (smoothed) − $C_{p,\mathrm{m}}$ (literature)]/$C_{p,\mathrm{m}}$ (smoothed). Horizontal line, our data as from ref 28; ○, ref 29; ◇, ref 30; △, ref 31; □, ref 32.

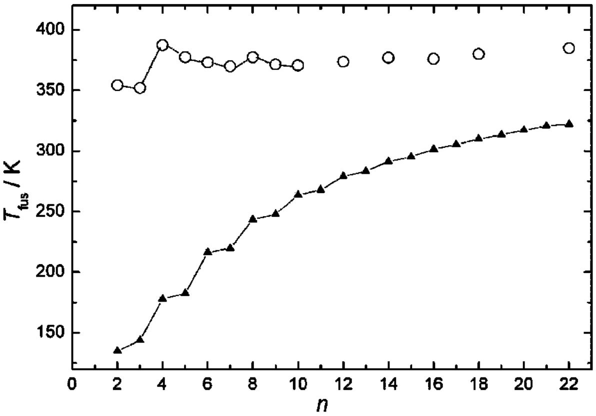

Figure 2. Temperatures of fusion T_{fus} as a function of the number of carbon atoms in the molecule: ○, alkylamides $H_3C-(CH_2)_{(n-2)}-CONH_2$; ▲, isoelectronic linear alkanes $H_3C-(CH_2)_n-CH_3$. T_{fus} values for C_7, C_9, and C_{14} are from ref 15 and that of C_2 is from ref 11.

manufacturer through accurate temperature measurements with a thermal sensor in the place of the sample crucible during several scanning runs at different heating rates. Heat corresponding to the experimental DSC peaks was determined by comparing their areas with others of approximately the same magnitude whose associated heat was obtained from both the sensitivity s of the heat flux detector and chart speed of the recorder, the former being expressed by the equation

$$s/(\mu\mathrm{V}\cdot\mathrm{mW}^{-1}) = 6.057 + 1.483\cdot10^{-2}\cdot(\langle T_{\mathrm{p}}\rangle - 298.15)/\mathrm{K} - 3.772\cdot10^{-5}\cdot\{(\langle T_{\mathrm{p}}\rangle - 298.15)/\mathrm{K}\}2 + 3.934\cdot10^{-8}\cdot\{(\langle T_{\mathrm{p}}\rangle - 298.15)/\mathrm{K}\}3 - 1.820\cdot10^{-11}\cdot\{(\langle T_{\mathrm{p}}\rangle - 298.15)/\mathrm{K}\}4 \quad (2)$$

where $\langle T_{\mathrm{p}}\rangle$ is the average temperature of the examined DSC peak, measured by the thermal sensor of the programmer. The sensitivity s of the heat flux detector as a function of temperature was determined by the manufacturer through a series of calibration runs using the Joule effect in the working temperature interval of the calorimeter T = (180 to 1100) K.

Several melting runs with gallium and indium were performed under the same conditions as the experimental determinations and showed agreement with the certified values for indium and IUPAC recommended values[20] for gallium. The accuracy was within 0.08 % for temperature and 0.25 % for enthalpy (Table 2).

Enthalpy and temperature calibrations of the Mettler DSC 30 apparatus were made through two built-in programs according to the procedure scheduled by the supplier.[22] The actual temperature of the phase transition of the samples at various scanning rates was established through a built-in program based on the melting points of three selected standards, indium, water, and hexane. The reference value for indium (429.75 K) was suggested by the supplier, in excellent agreement with that

Table 3. Temperatures and Molar Enthalpies and Entropies of Solid−Solid Transition and Fusion of the Primary Alkylamides[a]

			$\Delta_{trs}H_m$		T_{fus}/K		$\Delta_{fus}H_m$	$\Delta_{fus}S_m$
compound	N^b	T_{trs}/K	(kJ·mol^{-1})	N^b	this work	literature	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
propanamide				4	352.6 ± 0.3^{c}	352.8^{e}	12.9 ± 0.5^{c}	36.7 ± 0.4^{c}
butanamide				4	387.3 ± 0.4^{c}	388.8^{e}	19.2 ± 0.6^{c}	49.7 ± 0.5^{c}
				2	387.4 ± 0.1^{d}		19.6 ± 0.1^{d}	50.5 ± 0.2^{d}
2-methylpropanamide				2	400.1 ± 0.1^{d}		19.2 ± 0.1^{d}	48.0 ± 0.1^{d}
				3	400.4 ± 0.1^{c}		19.3 ± 0.1^{c}	48.2 ± 0.1^{c}
pentanamide	2	211.8 ± 0.3^{d}	1.9 ± 0.1^{d}					
	3	365.0 ± 0.4^{c}	1.20 ± 0.01^{c}	3	377.2 ± 0.1^{d}	379.0^{e}	17.9 ± 0.1^{d}	47.4 ± 0.1^{d}
	3	365.4 ± 0.1^{d}	1.06 ± 0.02^{d}	3	376.7 ± 0.4^{c}		19.3 ± 0.6^{c}	51.3 ± 0.6^{c}
2,2-dimethylpropanamide				4	425.4 ± 0.1^{d}		24.1 ± 0.3^{d}	56.8 ± 0.8^{d}
				4	425.6 ± 0.1^{c}		25.6 ± 0.1^{c}	60.2 ± 0.1^{c}
hexanamide	4	305.1 ± 0.1^{d}	7.9 ± 0.2^{d}	4	373.0 ± 0.1^{d}	373.8^{e}	16.7 ± 0.3^{d}	44.9 ± 0.7^{d}
	4	306.0 ± 0.3^{c}	7.9 ± 0.1^{c}	4	373.0 ± 0.4^{c}		17.6 ± 0.2^{c}	45.8 ± 0.5^{c}
octanamide	3	194.4 ± 0.7^{d}	1.91 ± 0.04^{d}					
	3	304.5 ± 0.3^{c}	0.97 ± 0.01^{c}	3	377.0 ± 0.4^{c}	378.8^{e}	27.6 ± 0.3^{c}	74.2 ± 0.7^{c}
	3	304.5 ± 0.1^{d}	0.99 ± 0.01^{d}	3	377.7 ± 0.1^{d}		27.2 ± 0.2^{d}	72.0 ± 0.6^{d}
decanamide	3	218.7 ± 0.2^{c}	1.05 ± 0.01^{c}	3	370.6 ± 0.3^{c}	371.6^{e}	15.1 ± 0.2^{c}	40.7 ± 0.4^{c}
	3	218.7 ± 0.1^{d}	1.05 ± 0.03^{d}	3	370.9 ± 0.1^{d}		17.4 ± 0.4^{d}	47.0 ± 1.0^{d}
	3	366.3 ± 0.4^{c}	18.8 ± 0.2^{c}					
	2	366.9 ± 0.2^{d}	21.1 ± 0.2^{d}					
dodecanamide	5	321.1 ± 0.1^{d}	9.7 ± 0.1^{d}	3	373.3 ± 0.1^{d}	375.3^{e}	36.3 ± 0.3^{d}	97.2 ± 0.8^{d}
	4	322.0 ± 0.3^{c}	9.0 ± 0.1^{c}	3	373.8 ± 0.4^{c}		35.7 ± 0.4^{c}	95.9 ± 0.9^{c}
hexadecanamide	3	355.5 ± 0.3^{c}	10.4 ± 0.1^{c}	3	376.0 ± 0.3^{c}	380.7^{e}	45.4 ± 0.4^{c}	115.5 ± 1.0^{c}
	3	356.1 ± 0.1^{d}	10.3 ± 0.3^{d}	3	375.6 ± 0.3^{d}		45.2 ± 0.3^{d}	120.4 ± 0.7^{d}
octadecanamide	4	298.7 ± 0.3^{c}	2.2 ± 0.1^{c}	2	379.7 ± 0.1^{d}	377.2^{f}	54.8 ± 0.8^{d}	144.4 ± 2.2^{d}
				4	380.0 ± 0.4^{c}	379.1^{g}	55.1 ± 0.6^{c}	145.3 ± 1.5^{c}
						382.2^{e}	59.9^{f} (lit.)	
docosanamide				2	383.3 ± 0.1^{d}		63.3 ± 0.3^{d}	165.0 ± 0.9^{d}
				3	384.9 ± 0.4^{c}		64.7 ± 0.7^{c}	168.2 ± 1.7^{c}

[a] Uncertainties are expressed as twice the standard deviation of the mean. [b] N = number of calorimetric runs. [c] Values obtained with the Setaram DSC 111. [d] Values obtained with the Mettler DSC 30. [e] Ref 16. [f] Ref 13. [g] Ref 14.

Table 4. Molar Heat Capacities $C_{p,m}$ for the Primary Alkylamides at Selected Temperatures[a]

	$C_{p,m}$/(J·K^{-1}·mol^{-1})									
T/K	C_4	i-C_4	C_5	t-C_5	C_6	C_8	C_{10}	C_{12}	C_{16}	C_{18}	C_{22}
183	96.4 ± 0.7	100.8 ± 0.6	111.5 ± 0.2		119.1 ± 0.6	164.7 ± 0.3					
188	98.3 ± 0.8	102.9 ± 0.9	116.1 ± 0.3	115.7 ± 0.7	121.1 ± 0.8	169.0 ± 0.7					
193	101.7 ± 0.9	105.0 ± 0.5	118.5 ± 0.8	117.6 ± 0.5	126.6 ± 0.6	174.2 ± 0.5					
198	104.1 ± 0.6	107.1 ± 0.5	122.5 ± 0.2	120.8 ± 0.9	128.6 ± 0.4	180.6 ± 0.5		213.3 ± 0.7			
203	106.4 ± 0.5	110.5 ± 0.9	128.9 ± 0.1	123.0 ± 0.7	132.5 ± 0.7	189.7 ± 0.4		217.8 ± 0.9			
208	108.0 ± 0.6	112.4 ± 0.8	133.1 ± 0.5	124.8 ± 0.9	135.8 ± 0.5	197.1 ± 0.7		223.3 ± 0.9	267.5 ± 1.0	318.2 ± 0.9	
213	109.7 ± 0.6	114.0 ± 0.8	139.1 ± 0.2	126.4 ± 0.5	138.8 ± 0.5	204.6 ± 0.7		227.1 ± 0.9	273.7 ± 1.3	328.5 ± 1.0	
218	112.5 ± 0.9	115.6 ± 0.9	145.1 ± 0.3	129.1 ± 0.6	142.1 ± 0.3	213.2 ± 0.5		231.8 ± 0.9	276.5 ± 1.2	336.6 ± 0.7	
223	114.3 ± 0.9	118.7 ± 0.6	154.0 ± 0.6	131.5 ± 0.5	146.7 ± 0.5	224.4 ± 0.5		237.5 ± 0.8	282.8 ± 1.0	345.2 ± 0.7	
228	116.0 ± 0.7	120.3 ± 0.4	162.5 ± 0.1	133.4 ± 0.9	150.8 ± 0.3	228.2 ± 0.3		242.2 ± 0.9	289.0 ± 1.2	353.1 ± 0.9	420.4 ± 1.3
233	118.1 ± 0.6	122.8 ± 0.8	175.0 ± 0.5	136.6 ± 0.5	155.3 ± 0.4	232.8 ± 0.8		245.9 ± 0.8	297.1 ± 1.1	360.8 ± 0.8	431.8 ± 1.1
238	120.8 ± 0.8	124.8 ± 0.4	183.4 ± 0.5	137.9 ± 0.5	160.1 ± 0.4	234.3 ± 0.6		251.2 ± 0.9	302.6 ± 1.2	367.6 ± 0.9	439.8 ± 1.2
243	123.0 ± 0.8	127.3 ± 0.8	195.4 ± 0.7	140.2 ± 0.8	165.6 ± 0.6	235.1 ± 0.7		258.4 ± 0.7	310.3 ± 0.9	375.8 ± 0.6	449.2 ± 1.1
248	125.9 ± 0.8	130.8 ± 0.3	200.8 ± 0.2	142.8 ± 0.5	169.6 ± 0.5	236.3 ± 0.9		263.0 ± 0.8	319.5 ± 1.1	385.6 ± 0.9	461.3 ± 0.9
253	127.4 ± 0.8	132.6 ± 0.9	199.8 ± 0.2	144.5 ± 0.9	173.1 ± 0.8	233.9 ± 0.5		269.2 ± 0.8	323.8 ± 1.2	393.6 ± 1.1	470.1 ± 0.8
258	130.2 ± 0.6	134.6 ± 0.8	196.2 ± 0.3	147.5 ± 0.6		236.1 ± 0.9		274.3 ± 0.8	331.6 ± 1.3	403.2 ± 1.0	480.5 ± 0.8
263	132.4 ± 0.9	137.6 ± 0.9	191.6 ± 0.8	149.2 ± 0.8		238.3 ± 0.6	236.4 ± 0.8	280.8 ± 0.6	340.1 ± 1.3		493.0 ± 0.8
268	135.0 ± 0.4	138.8 ± 0.9	185.8 ± 0.9	150.9 ± 0.6		235.4 ± 0.9	238.5 ± 0.6		348.1 ± 1.2		500.2 ± 1.2
273	136.8 ± 0.9	141.9 ± 0.9	189.4 ± 0.5	153.8 ± 0.8		241.2 ± 0.5	247.6 ± 0.8		357.9 ± 1.1		511.9 ± 0.7
278	139.3 ± 0.7	144.6 ± 0.8	187.1 ± 0.6	156.3 ± 0.5		242.7 ± 0.8	251.1 ± 0.6		364.8 ± 1.4		523.7 ± 1.2
283	141.5 ± 0.9	146.5 ± 0.6	188.4 ± 0.7	158.3 ± 0.5		243.9 ± 0.8	260.7 ± 0.5		371.6 ± 1.3		539.7 ± 1.1
288	143.7 ± 0.7	148.5 ± 0.8	188.4 ± 0.7	161.1 ± 0.6		244.9 ± 0.5	266.4 ± 0.7		378.1 ± 1.3		548.1 ± 0.5
293	146.4 ± 0.8	150.9 ± 0.6	190.0 ± 0.8	163.0 ± 0.7		246.5 ± 0.7	270.2 ± 0.7		387.6 ± 1.1		561.1 ± 1.3
298	147.7 ± 0.5	152.4 ± 0.8	190.3 ± 0.3	163.7 ± 0.7		245.1 ± 0.7	272.4 ± 0.4		394.3 ± 1.1		568.7 ± 1.4
303	150.3 ± 0.6	154.1 ± 0.9	192.6 ± 0.7	165.4 ± 0.7		246.7 ± 0.6	278.5 ± 0.3		401.8 ± 1.4		
308	153.5 ± 0.6	158.0 ± 0.7	196.4 ± 0.8	167.9 ± 0.6		249.3 ± 0.5	287.0 ± 0.5				
313	155.0 ± 0.5	160.2 ± 0.5	198.4 ± 0.9	170.2 ± 0.5		251.8 ± 0.9	291.6 ± 0.7				
318	158.8 ± 0.7	162.7 ± 0.9	202.5 ± 0.7	172.7 ± 0.6			297.9 ± 0.9				
323	161.4 ± 0.5	164.5 ± 0.9	204.5 ± 0.5	174.2 ± 0.6			304.4 ± 0.8				

[a] Uncertainties are expressed as twice the standard deviation of the mean.

recommended by IUPAC,[20] while values for hexane (178.06 K) and water (273.16 K) were selected from the literature.[23–27] The program compares the instrumental response with the reference temperature values and provides an appropriate set of calibration parameters in the temperature interval of interest, T = (180 to 430) K. Enthalpy change was calibrated through a second built-in program based on the enthalpy of fusion of indium incorporated by Mettler (3.267 kJ·mol^{-1}), in very good agreement with that of (3.273 ± 0.022) kJ·mol^{-1} from the latest IUPAC compilation on reference materials for enthalpy mea-

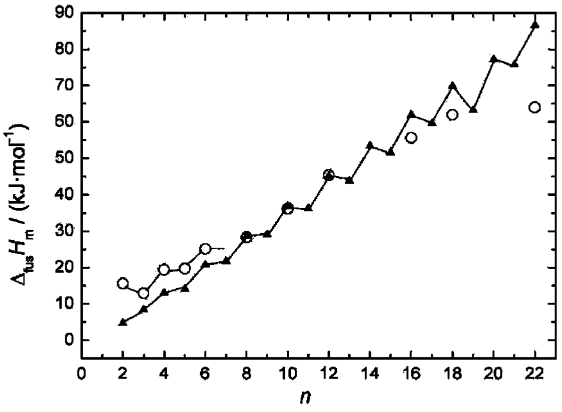

Figure 3. Molar enthalpies of fusion $\Delta_{fus}H_m$ as a function of the number of carbon atoms in the molecule: ○, alkylamides $H_3C-(CH_2)_{(n-2)}-CONH_2$; ▲, isoelectronic linear alkanes $H_3C-(CH_2)_n-CH_3$.

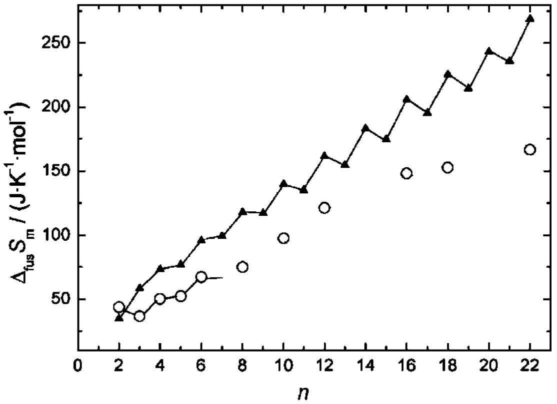

Figure 4. Molar entropies of fusion $\Delta_{fus}S_m$ as a function of the number of carbon atoms in the molecule: ○, alkylamides $H_3C-(CH_2)_{(n-2)}-CONH_2$; ▲, isoelectronic linear alkanes $H_3C-(CH_2)_n-CH_3$.

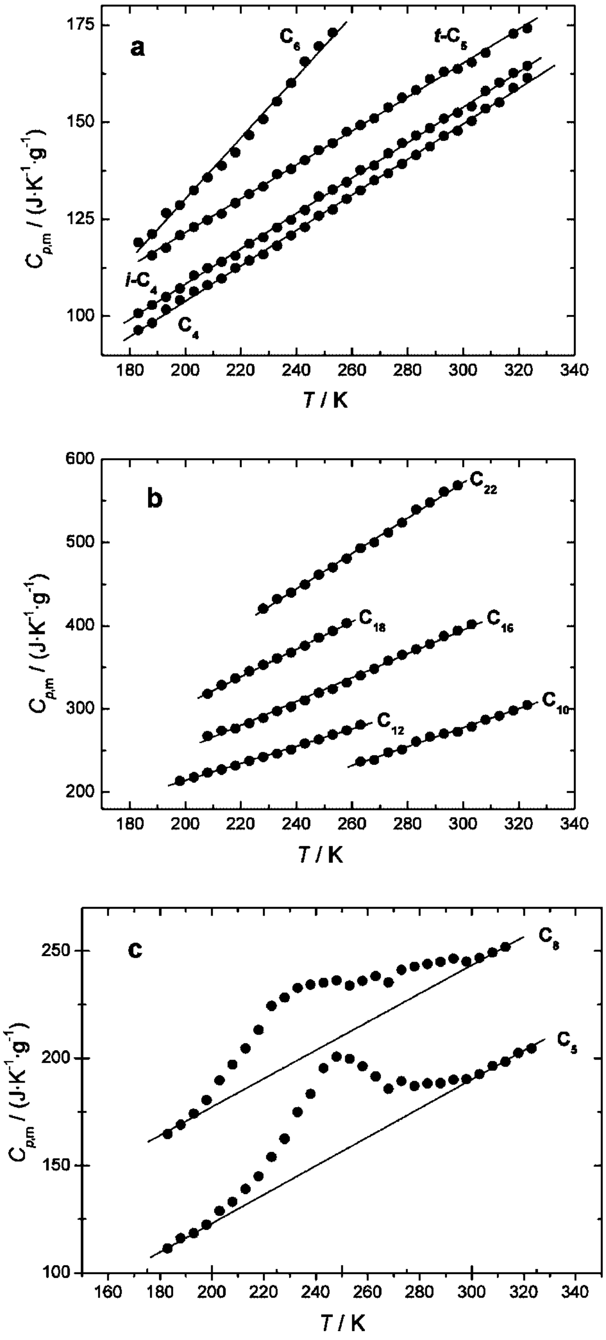

Figure 5. Molar heat capacities $C_{p,m}$ of the alkylamides as a function of temperature: ●, experimental and — smoothed data: (a) butanamide (C_4), 2-methylpropanamide (i-C_4), 2,2-dimethylpropanamide (t-C_5), hexanamide (C_6); (b) decanamide (C_{10}), dodecanamide (C_{12}), hexadecanamide (C_{16}), octadecanamide (C_{18}), docosanamide (C_{22}); (c) pentanamide (C_5), octanamide (C_8).

surements.[20] Additional runs with naphthalene and octane were made to check both the accuracy and precision of our DSC Mettler 30 apparatus (Table 2).

Measurements with the Setaram DSC 111 were performed in sealed stainless steel crucibles and static air condition, while sealed aluminum crucibles and nitrogen as purge gas (flow rate $7 \cdot 10^{-4}$ dm^3·s^{-1}) were used with the Mettler DSC 30. Three or more fresh samples of each alkylamide were analyzed with both apparatuses. After melting, the samples were cooled to the starting temperature and then additional heating runs were performed to check the reversibility of the solid−solid transitions.

Heat Capacity Measurement. Heat-flow rate calibration of the Mettler DSC 30 calorimeter coupled with a Mettler TC 10A processor was made with benzoic acid, the reference material recommended for organic compounds, in the temperature range $T = (180 \text{ to } 350)$ K.[20] Pellets of about $3 \cdot 10^{-2}$ g, exactly fitting into the aluminum calorimetric crucibles, sealed aluminum crucibles of $4 \cdot 10^{-5}$ dm^3, nitrogen as purge gas (flow rate $7 \cdot 10^{-4}$ dm^3·s^{-1}), and a heating rate of 166.7 mK·s^{-1} were used. These conditions were selected after investigations concerning the best conditions for good repeatability of experimental data and correctness of $C_{p,m}$ values at 298.15 K as a function of sample mass and DSC heating rate.[28] A blank method was used for C_p determinations: a run with an empty crucible in the place of the sample and another empty crucible as the reference was performed and baseline; i.e., the "blank" was stored in a specific built-in program of the TC 10A processor that subtracts it from each experimental curve and provides instrumental $C_{p,m}$ values as a function of temperature. The average values in 5 K intervals were compared with the corresponding smoothed $C_{p,m}$ values from ref 20. A set of heat-flow rate conversion factors were thus obtained at various temperatures. The molar heat capacity of urea, as the internal reference material, was measured to check our entire calibration procedure. The deviation of the experimental results from the smoothed curve values was within ± 0.2 %. The heat capacity against temperature linear fit for urea[28] (horizontal line) compared with the literature[29–32] in the range $T = (180 \text{ to } 360)$ K shows that our equation provides a good average for the various series of data (Figure 1). Moreover, our

Table 5. Molar Heat Capacities of the Primary Alkylamides at 298.15 K as a Function of Temperature from Equation 3

compound	T/K	N_s[a]	N_r[b]	A[c]	B[c]	r[d]
butanamide	183 to 323	2	4	148.5 ± 0.2	0.454 ± 0.003	0.9990
2-methylpropanamide	183 to 323	2	4	153.0 ± 0.2	0.458 ± 0.002	0.9993
pentanamide	183 to 323	2	4	189.1 ± 0.3[e]		
2,2-dimethylpropanamide	188 to 323	3	6	164.2 ± 0.2	0.436 ± 0.003	0.9989
hexanamide	183 to 253	2	4	207.0 ± 1.5[f]	0.78 ± 0.02	0.9933
octanamide	183 to 313	2	4	242.5 ± 0.4[e]		
decanamide	263 to 323	3	6	275.1 ± 0.5	1.13 ± 0.03	0.9935
dodecanamide	198 to 263	2	4	314.9 ± 1.1[f]	1.03 ± 0.02	0.9972
hexadecanamide	208 to 303	3	6	392.7 ± 1.1	1.45 ± 0.02	0.9964
octadecanamide	208 to 258	2	4	468.0 ± 1.3[f]	1.65 ± 0.02	0.9988
docosanamide	228 to 298	2	5	567.8 ± 1.3	2.12 ± 0.03	0.9972

[a] Number of samples. [b] Number of DSC runs. [c] Uncertainties at 95 % level of confidence. [d] Product-moment correlation coefficient. [e] Interpolated values (drawn baseline). [f] Extrapolated values.

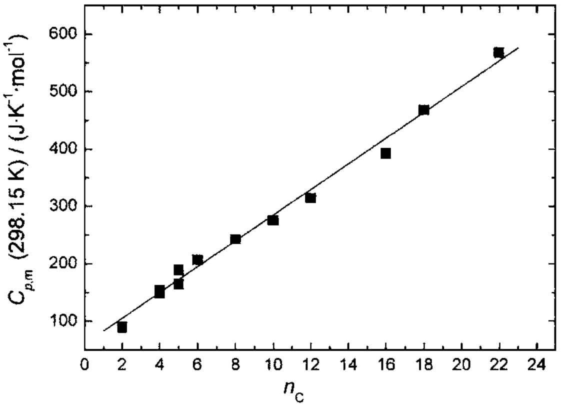

Figure 6. Molar heat capacities $C_{p,m}$ of alkylamides at $T = 298.15$ K as a function of the number of carbon atoms in the molecule. $C_{p,m}$ at 298.15 K for acetamide ($n_C = 2$) is from ref 46.

Table 6. CH_2 Group Contribution to Molar Heat Capacity at 298.15 K of the Primary Alkylamides and Various Alkyl Compounds

compound	n[a]	n_c[b]	$C_{p,m}$/ (J·K^{-1}·mol^{-1})	references
alkylamides	11	4 to 22	22.5 ± 0.7	this work
alkane-α,ω-diamides	12	2 to 12, 14	22.6 ± 0.4	ref 28
alkane-α,ω-diols	12	2 to 16	22.5 ± 0.6	refs 47 to 49
alkan-1-ols	13	1 to 16	22.9 ± 0.6	refs 50 to 55
alkanoic acids	12	7 to 20	20.6 ± 0.7	refs 56, 57
alkanes	22	4 to 33	22.5 ± 0.4	refs 23, 24, 58

[a] Number of compounds in the series. [b] Number of carbon atoms of the compounds at the extremities of the series.

$C_{p,m}$ at 298.15 K (91.8 J·K^{-1}·mol^{-1}) is in very good agreement with our earlier value obtained by DSC (91.0 J·K^{-1}·mol^{-1})[29] and in accordance with the average value (92.1 J·K^{-1}·mol^{-1}) of three adiabatic measurements reported in the literature.[30–32]

The molar heat capacities of the alkylamides were determined at $T = (183$ to $323)$ K in the same experimental conditions employed for the heat flow rate calibration. Experimental heat flow rates were taken in 5 K intervals, and values of four to six determinations per alkylamide, using two pellets and performing at least two DSC runs each, were averaged at the selected temperatures.

Results and Discussion

Solid−Solid and Solid−Liquid Phase Transitions. The experimental temperatures and enthalpies and the derived entropies of fusion and solid-to-solid transitions for the 11 alkylamides are presented in Table 3, together with the current literature values. It is worth mentioning that the literature T_{fus} values were determined by Kjeldhal, except for acetamide and octadecanamide. In Figure 2, the fusion temperatures are shown as a function of the number of carbon atoms in alkylamide molecules and compared with the almost isoelectronic linear alkanes.[33] The higher T_{fus} alkylamide values are due to the presence of H-bond and dipole–dipole interactions, whereas only dispersion forces are present in alkanes. T_{fus} alternation regularly manifests from C_6 to C_{10} with C_4 and C_5 showing the highest values of the even and odd terms of the series, respectively. Alkanes and mono- or terminally bifunctional alkylderivatives display remarkable alternation of fusion temperatures with even terms systematically exhibiting higher values than odd terms.[34–37] Recently, we found that temperature, enthalpy, and entropy of fusion of diamines, diamides, and dinitriles exhibit alternating behavior.[8–10] In most cases, odd–even alternation is related with the alkyl interchain and terminal groups packing in the solid phase. For alkylamides, a common crystal arrangement was reported for C_3 to C_{16} since they belong to the same space group, P2$_1$/a, except nonanamide (space group A2/a), with centrosymmetric hydrogen-bonded pairs, the centers of which coincide with centers of symmetry of the unit cell.[38–42] Centrosymmetric dimers are formed through a pair of N−H···O hydrogen bonds, whereas the other amine H atoms are used to link adjacent dimers through N−H···O hydrogen bonds, resulting in the formation of a three-dimensional structure.[38,39,41] Exceptions to this rule include both the orthorhombic and rhombohedral forms of acetamide in which the pair is only pseudocentrosymmetric or the hydrogen-bonded pairs are not formed.[43,44] Although there is no indication of differences in the molecular packing of the crystalline alkylamides, the X-ray diffraction study of Wurz and Sharpless[45] showed a marked similarity of structure between even terms from C_8 to C_{14} and odd terms from C_7 to C_{13}. In addition, Turner and Lingafelter determined the effective cross-sectional areas in alkylamide crystals which indicate a looser packing in odd terms.[38] Therefore, odd–even alternation of alkylamides T_{fus} can be ascribed to differences in the closeness of packing in even and odd terms.

In Figure 3, the molar enthalpies of fusion, $\Delta_{fus}H_m$, are reported as a function of the number of carbon atoms n and compared with those of the nearly isoelectronic alkanes.[33] The trend displayed by alkylamide $\Delta_{fus}H_m$ values almost overlaps the alkane pattern. However, different behaviors can be distinguished: for C_2 to C_6, fusion enthalpies are slightly higher than those of the corresponding alkanes, then practically coincide for C_8, C_{10}, and C_{12}, and become lower for C_{16}, C_{18}, and C_{22}. In particular, even terms C_4 and C_6 display values slightly higher than the odd terms C_3 and C_5. Unfortunately, the lack of other commercial odd alkylamides prevented us from continuing the comparison of fusion enthalpies we obtained for higher even terms. Syntheses of odd alkylamides from C_7 to C_{15} are now in the course.

An odd–even effect in sublimation enthalpies of alkylamides was already reported by Davies et al.[15] Moreover, they observed a marked discontinuity at C_8-C_{10} in both the increment of molecular volumes and sublimation enthalpies and attributed it to a change in packing in the neighborhood of C_8 in the even amides. We found a similar behavior for both fusion enthalpy and entropy patterns (Figures 3 and 4).

Our thermodynamic fusion data confirm the existence of structural factors inducing changes in the alkylamide lattice energies between even and odd terms, as well as between lower and higher even terms.

The lower than expected entropies of fusion (Figure 4) can be ascribed to the persistence in the liquid phase of hydrogen bonds that establish intermolecular associations, confirmed by the high dielectric constants of these liquids.[16]

Heat Capacity. In Table 4, the averaged values of molar heat capacities, $C_{p,\mathrm{m}}$, of alkylamides in the interval $T = (183 \text{ to } 323)$ K are presented. They increased linearly as a function of temperature, and linear fits (Figures 5a and 5b) were used to derive values at 298.15 K

$$C_{p,\mathrm{m}}/(\mathrm{J\cdot K^{-1}\cdot mol^{-1}}) = A + B(T/\mathrm{K} - 298.15), \quad \text{where } A = C_{p,\mathrm{m}}(298.15\ \mathrm{K}) \quad (3)$$

The standard deviations of experimental molar heat capacities from the smoothed heat capacities calculated by eq 3 were within ± 0.4 %, except for some points around the lower and upper temperature limits. Since solid−solid transitions have been detected for C_6, C_{10}, C_{12}, and C_{18} (Table 3), reduced temperature ranges were used for these compounds. For C_6, C_{10}, and C_{18}, $C_{p,\mathrm{m}}$ values were obtained by extrapolation to 298.15 K. For C_5 and C_8, smooth solid−solid transitions covering a relatively large interval of temperature requested that $C_{p,\mathrm{m}}(298.15\ \mathrm{K})$ be derived from a drawn baseline (Figure 5c).

In Table 5, the intercepts *A*, slopes *B*, and product-moment correlation coefficients *r* for each compound are listed. The only two $C_{p,\mathrm{m}}$ values at 298.15 K in the literature,[15] 148.1 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for 2-methylpropanamide and 159.8 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ for 2,2-dimethylpropanamide, are close to those determined in the present work. The $C_{p,\mathrm{m}}(298.15\ \mathrm{K})$ values displayed a linear dependence on the carbon atom number in the molecule (Figure 6), with a slope of $(22.5 \pm 0.7)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. This value represents the average experimental $C_{p,\mathrm{m}}$ contribution of the CH_2 group in linear alkylamides that practically coincides with our earlier values for 12 linear alkane-α,ω-diamides[28] and ten alkane-α,ω-diols[47] (Table 6). It is also in very good agreement with that estimated by Domalski and Hearing,[59] even though the $C_{p,\mathrm{m}}$ values estimated for butanamide, pentanamide, hexanamide, octanamide, 2-methylpropanamide, and 2,2-dimethylpropanamide are lower than our values.

Acknowledgment

E. Badea, on leave from the University of Craiova, Romania, is grateful to the University of Torino for research contracts within the compass of EU projects.

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Received for review November 13, 2007. Accepted February 4, 2008. This research was partially funded by the Ministero dell'Università e della Ricerca (Mi.U.R.).

JE700662A