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HEAT CAPACITIES OF A SERIES OF TERMINAL LINEAR ALKYLDIAMIDES DETERMINED BY DSC

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Molar heat capacities of twelve linear alkane-α,ω-diamides $H_2NOC–(CH_2)_{(n–2)}–CONH_2$, ($n$=2 to 12 and n=14) were measured by differential scanning calorimetry at T=183 to 323 K. Heat flow rate calibration of the Mettler DSC 30 calorimeter was carried out by using benzoic acid as reference material. The calibration was checked by determining the molar heat capacity of urea in the same temperature range as that of measurements. The molar heat capacities of alkane-α,ω-diamides increased in function of temperature and fitted into linear equations. Smoothed values of $C_{p,m}$ at 298.15 K displayed a linear increase with the number of carbon atoms. The $C_{p,m}$ contribution of CH_2 group was (22.6±0.4) J $K^{–1}$ $mol^{–1}$, in agreement with our previous results concerning linear alkane-a,ω-diols and primary alkylamides as well as the literature data on various series of linear alkyl compounds.

Keywords: *alkyldiamides, differential scanning calorimetry, methylene group contribution, molar heat capacity*

Introduction

Precise evaluation of the molar heat capacity as a function of temperature is fundamental in many thermodynamic calculations concerning the structure and stability of organic compounds. In particular, molar heat capacities are used to derive enthalpies and entropies of sublimation at 298.15 K and, hence, the enthalpies of solvation as well as the partial molar heat capacities of solution at infinite dilution [1–8]. We have investigated the thermodynamic properties, including molar heat capacity [9–14] of homologous series of solid and liquid organic compounds acting as biochemical model molecules. It should be noted that some group additivity methods have also been developed for the estimation of condensed phase heat capacity [15–19].

Alkane-α,ω-diamides (hereinafter named alkyldiamides) are simple organic compounds characterised by both hydrogen bonding and dispersive forces typical of the ubiquitous interactions within biological structures.

In this work we determined the molar heat capacities, $C_{p,m}$, in the temperature range T=183 to 323 K for twelve linear alkyldiamides $H_2NOC–(CH_2)_{(n–2)}–CONH_2$, with n=2 to 12 and n=14, where n= number of carbon atoms in the parent dicarboxylic alkanoic acid. The measurements were performed by differential scanning calorimetry (DSC). The calorimeter was accurately calibrated to ensure reliable $C_{p,m}$ values. In addition, the contribution to heat capacity of the methylene group in alkyldiamides was derived and compared to other values obtained from various series of alkyl compounds previously studied by some of us or found in the literature.

The thermodynamic properties of alkyldiamides have received little attention in the literature. No heat capacities of solid terminal alkyldiamides are available, except for oxalamide and malonamide at T=298.15 K, and succinamide at 323 K. The heat capacity of oxalamide was measured with a low temperature calorimeter at T=10 to 310 K by Egan *et al.* [20], and Imamura *et al.* have provided that of malonamide by using the DSC continuous-heating method [21]. A $C_{p,m}$ value at T=323 K of succinamide was reported by Satoh and Sogabe [22].

We have previously studied solid-to-liquid and solid-to-solid phase transitions of alkyldiamides [23]. Further work on the vaporisation behaviour of alkyldiamides has now been accomplished to complete their thermodynamic characterisation by providing enthalpies and entropies of sublimation [24].

Experimental

Materials

The homologous series of twelve alkane-α,ω-diamides $H_2NOC–(CH_2)_{(n–2)}–CONH_2$ examined in this work are listed in Table 1, with their formulae, number of

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Table 1 List of the alkane-α,ω-diamides with their formulae, number of carbon atoms in the molecule, n_C, adopted symbols, molar masses, *M*, and origin

Compound	Formula	n_C	Symbol	M^a/g mol^{-1}	Origin
Ethanediamide (oxalamide)	$H_2NOC–CONH_2$	2	C_2	88.066	Fluka
Propanediamide (malonamide)	$H_2NOC–CH_2–CONH_2$	3	C_3	102.092	Fluka
Butanediamide (succinamide)	$H_2NOC–(CH_2)_2–CONH_2$	4	C_4	116.119	Fluka
Pentanediamide (glutaramide)	$H_2NOC–(CH_2)_3–CONH_2$	5	C_5	130.146	synthesis[b]
Hexanediamide (adipamide)	$H_2NOC–(CH_2)_4–CONH_2$	6	C_6	144.173	Aldrich
Heptanediamide (pimelamide)	$H_2NOC–(CH_2)_5–CONH_2$	7	C_7	158.200	synthesis[b]
Octanediamide (suberamide)	$H_2NOC–(CH_2)_6–CONH_2$	8	C_8	172.226	synthesis[b]
Nonanediamide (azelamide)	$H_2NOC–(CH_2)_7–CONH_2$	9	C_9	186.253	synthesis[b]
Decanediamide (sebacamide)	$H_2NOC–(CH_2)_8–CONH_2$	10	C_{10}	200.280	synthesis[b]
Undecanediamide	$H_2NOC–(CH_2)_9–CONH_2$	11	C_{11}	214.307	synthesis[b]
Dodecanediamide	$H_2NOC–(CH_2)_{10}–CONH_2$	12	C_{12}	228.334	synthesis[b]
Tetradecanediamide	$H_2NOC–(CH_2)_{12}–CONH_2$	14	C_{14}	256.387	synthesis[b]

[a] Based on the 1999 IUPAC table of standard atomic masses of the elements and its 2001 revision [23]
[b] Syntheses made in our laboratory by hydrolysis of the parent terminal dinitriles

carbon atoms in the molecule, symbols adopted, molar masses and commercial origins. Four diamides were commercial products from Fluka and Aldrich. The other eight were synthesised in our laboratory by hydrolysis of the parent alkane-α,ω-dinitriles. Tridecanediamide was not prepared since its parent dinitrile is commercially unavailable. Alkyldiamides were purified by successive crystallisations from appropriate solutions with solvents, such as ethanol, ethylacetate, water and acetylacetone. The preparation and purification procedures are described in detail in [23]. The final purity of compounds was always better than 99%, as determined by the DSC peak profile method [26]. Their NMR spectra were in very good agreement with literature.

Indium (SRM 758) from NIST, hexane (GC standard, mass fraction ≥0.997) from Fluka and water (mass fraction 0.99999) from Aldrich were used as reference materials for temperature calibration. Indium was also used for enthalpy calibration of the Mettler DSC30 calorimeter according to the manufacturer's protocol [27]. Heat flow rate calibration was performed with benzoic acid (CRM No. M16-06, mass fraction 0.9999) from NPL [28]. Urea (SRM 2152) from NIST was used to check the correctness of our calibration procedure under the conditions adopted for C_p measurements. Nitrogen (mass fraction 0.99999) from Air Liquide Italia s.r.l. was employed as purge gas in all DSC runs.

Differential scanning calorimetry

Measurements were made with a Mettler DSC 30 calorimeter coupled with a Mettler TC 10A processor. Enthalpy and temperature calibrations of the calorimeter were first made through two built-in programs following the procedure scheduled by the supplier [27]. Heat flow rate calibration was made with benzoic acid, which is a recommended reference material for $C_{p,m}$ measurements of solid organic compounds [29].

Heat capacities of samples were determined using sealed aluminium crucibles of $4\cdot10^{-5}$ dm^3 and nitrogen as purge gas (flow rate $7\cdot10^{-4}$ dm^3 s^{-1}). Pellets of about $3\cdot10^{-2}$ g, exactly fitting into the aluminium calorimetric crucibles, and heating rate of 166.7 mK s^{-1} were used for the experiments. These conditions were selected after investigations concerning 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. A blank method was used for C_p determinations: every day, a run with an

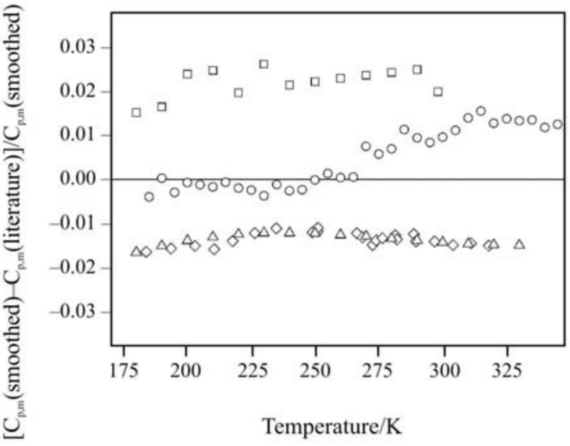

Fig. 1 Molar heat capacity of urea as a function of temperature: deviations of literature values from our data. Horizontal line, this work; ○ – [11]; ◇ – [30]; △ – [31]; □ – [32]

empty crucible in the place of the sample and another empty crucible as 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. Several runs with benzoic acid were carried out in the temperature range T=180 to 350 K and average values in 5 K intervals were compared with the corresponding smoothed $C_{p,m}$ values from [29]. A set of heat flow rate conversion factors was thus obtained at various temperatures. The molar heat capacity of urea, as internal reference material, was measured to check our entire calibration procedure. In Fig. 1, our smooth equation for urea (horizontal line) is compared with literature results [11, 30–32] in the range T=180 to 350 K and our equation satisfactorily averages various series of data. The observed deviation of about ±2% is ascribable to the intrinsic spreading out of various $C_{p,m}$ sets.

The molar heat capacity of alkyldiamides were determined in the interval T=183 to 323 K, following the experimental procedure selected for both calibration with benzoic acid and measurements of $C_{p,m}$ of urea. Experimental heat flow rates were taken in 5 K intervals, and values of six determinations (i.e. using two pellets and performing three DSC runs each) per alkyldiamide were averaged at the selected temperatures.

Results and discussion

In Tables 2 and 3, the molar heat capacities, $C_{p,m}$, of alkyldiamides at selected temperatures in the

Table 2 Molar heat capacities $C_{p,m}$ for C_2 to C_7 alkane-α,ω-diamides at selected temperatures

T/K	$C_{p,m}$/J K^{-1} mol^{-1}					
	C_2	C_3	C_4	C_5	C_6	C_7
183	75.76	90.43	104.96	109.00	136.33	146.97
188	77.36	92.43	108.19	113.15	139.95	151.64
193	78.79	94.13	109.09	114.43	141.30	154.17
198	80.26	96.73	110.88	116.77	144.53	158.62
203	81.07	98.24	113.98	119.35	146.69	162.98
208	82.83	99.98	116.07	122.07	149.90	167.22
213	84.93	102.02	118.38	125.08	152.68	170.53
218	86.14	103.66	120.76	128.30	155.34	174.92
223	88.12	105.79	123.41	131.38	159.30	179.28
228	89.72	107.76	125.36	134.15	161.77	182.12
233	91.33	110.20	128.11	136.93	165.09	186.40
238	93.07	111.63	130.45	138.48	167.89	189.51
243	94.95	113.16	132.76	140.75	170.39	192.28
248	96.06	115.13	134.63	143.72	174.55	196.32
253	97.61	116.69	137.38	146.71	176.70	200.12
258	99.51	118.57	140.24	149.46	178.98	203.83
263	100.67	120.08	142.63	151.64	182.01	207.57
268	101.53	121.60	143.99	154.36	184.69	209.74
273	102.93	124.13	146.70	158.30	187.71	215.69
278	104.05	126.35	148.72	159.57	190.43	219.02
283	106.23	128.45	150.90	163.99	193.88	223.68
288	107.36	130.39	153.76	166.04	196.93	226.82
293	109.37	131.60	155.87	167.87	200.54	229.77
298	110.86	133.38	158.17	170.21	203.50	230.82
303	112.13	135.53	160.39	172.85	205.09	234.22
308	114.30	137.64	164.32	175.49	210.25	237.83
313	115.72	139.20	165.75	178.76	212.93	242.77
318	115.94	140.95	167.97	181.91	215.64	245.93
323	118.75	143.50	170.55	185.11	220.16	250.96

Table 3 Molar heat capacities $C_{p,m}$ for C_8 to C_{14}, except C_{13}, alkane-α,ω-diamides at selected temperatures

T/K	$C_{p,m}$/JK^{-1} mol^{-1}					
	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{14}
183	159.19	171.22	190.27	208.14	210.75	244.92
188	166.00	176.47	197.84	214.91	215.08	252.03
193	169.87	179.10	201.97	220.94	219.62	256.19
198	173.32	183.18	207.24	226.20	224.66	263.97
203	176.88	188.98	212.49	231.59	231.42	269.08
208	180.14	193.04	216.98	234.93	237.06	275.86
213	184.10	197.10	221.43	239.06	241.40	283.04
218	188.27	202.58	224.60	244.10	246.85	288.63
223	192.49	207.16	229.51	249.13	252.92	296.59
228	195.86	212.23	234.11	252.95	257.90	302.69
233	199.39	216.83	238.23	257.62	263.17	307.68
238	202.61	220.18	240.54	261.85	268.70	311.93
243	206.55	223.81	243.57	266.55	272.94	318.09
248	209.25	229.85	248.39	270.14	277.38	323.45
253	213.17	233.86	252.96	274.78	280.98	328.98
258	217.37	238.00	257.63	279.05	287.35	336.56
263	221.79	243.34	262.49	285.67	292.40	343.33
268	223.99	245.60	264.70	286.97	296.59	346.70
273	229.62	250.92	271.20	294.40	304.52	355.39
278	232.34	256.29	274.87	298.90	309.89	361.17
283	236.65	261.32	280.51	304.74	315.46	367.67
288	239.59	265.10	284.54	308.25	321.31	374.24
293	243.31	269.23	287.92	313.05	324.01	379.34
298	245.33	270.30	289.66	314.53	327.84	383.31
303	248.79	274.72	294.62	319.54	333.14	387.81
308	252.86	279.58	299.84	324.55	336.96	396.34
313	256.87	285.48	306.41	331.85	346.81	404.65
318	262.08	289.34	309.54	336.38	350.85	409.48
323	266.17	296.53	317.08	344.20	358.75	418.60

temperature interval T=183 to 323 K are presented. They increased linearly as a function of temperature and linear fits were used to derive the molar heat capacity values at 298.15 K:

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

It should be stressed that in this temperature range no solid-to-solid transitions are present as recently reported [23].

In Table 4, the intercepts at T=298.15 K (A), slopes (B) and product-moment correlation coefficients (r) for each compound are listed. The only two $C_{p,m}$ values at 298.15 K found in the literature, 113.89 J K^{-1} mol^{-1} for oxalamide [20] and 124 J K^{-1} mol^{-1} for malonamide [21], are close to ours, while that reported for succinamide at 323 K [22], i.e. 174.0 J K^{-1} mol^{-1}, is in fair agreement with our experimental value 170.55 J K^{-1} mol^{-1} (Table 2).

The $C_{p,m}$ values of alkyldiamides at 298.15 K displayed a linear dependence as a function of their carbon atoms number (Fig. 2), with a slope of 22.6±0.4 J K^{-1} mol^{-1}. This value represents the average experimental $C_{p,m}$ contribution of the CH_2 group in linear alkyldiamides and practically coincides with that which we found for a series of ten alkane-α,ω-diols, 23.0±1.0 J K^{-1} mol^{-1} [14] and for a series of eleven linear primary alkylamides, 22.5±0.7 J K^{-1} mol^{-1} [33].

We used two group additivity schemes from the literature [15–19] to calculate $C_{p,m}$ of alkyldiamides. In [15, 16], the heat capacity contribution of the functional group $CONH_2$ at 298.15 K, $C_{p,m}$=54.4 J K^{-1} mol^{-1} corresponds to 50% of our value

Table 4 Molar heat capacities of the alkane-α,ω-diamides as a function of temperature from the equation: $C_{p,m}$/J K^{-1} mol^{-1}=A+B(T/K–298.15), where A=$C_{p,m}$(298.15 K)

Compound	T/K	N_S^a	N_r^b	A^c	B^c	r^d
Ethanediamide	183 to 323	2	3	110.9±0.1	0.305±0.002	0.9988
Propanediamide	183 to 323	2	3	133.7±0.1	0.374±0.002	0.9995
Butanediamide	183 to 323	2	3	158.5±0.1	0.469±0.002	0.9995
Pentanediamide	183 to 323	2	3	170.9±0.2	0.536±0.003	0.9992
Hexanediamide	183 to 323	2	3	203.3±0.2	0.591±0.004	0.9990
Heptanediamide	183 to 323	2	3	232.5±0.3	0.730±0.005	0.9986
Octanediamide	183 to 323	2	3	246.7±0.3	0.737±0.004	0.9991
Nonanediamide	183 to 323	2	3	272.7±0.3	0.879±0.005	0.9990
Decanediamide	183 to 323	2	3	292.3±0.4	0.856±0.007	0.9982
Undecanediamide	183 to 323	2	3	317.2±0.4	0.923±0.007	0.9985
Dodecanediamide	183 to 323	2	3	329.8±0.4	1.039±0.006	0.9990
Tetradecanediamide	183 to 323	2	3	385.2±0.4	1.215±0.006	0.9992

[a]Number of samples, [b]Number of DSC runs per sample, [c]Uncertainties at 95% confidence limits, [d]Product-moment correlation coefficient

for oxalamide, 110.9 J K^{-1} mol^{-1} (Table 4). However, the estimated contribution of the CH_2 group is higher than our experimental value. By contrast, $C_{p,m}$ (CH_2) at 298.15 K estimated in [17] is 21.92 J K^{-1} mol^{-1}, in very good agreement with our value as well as with a weighted mean of CH_2 group contributions, 22.1±0.5 J K^{-1} mol^{-1}, obtained from the experimental $C_{p,m}$ values for some homologous series of linear alkanes, alkan-1-ols and alkanoic acids [14]. However, the full contribution of the $CONH_2$ group is not given in [19] and that obtained from the sum of heat capacity contributions of CO and NH_2 single groups is far from our experimental value. In addition, the only $C_{p,m}$ value fully calculated in [19] for alkyldiamides is that of succinamide 90.84 J K^{-1} mol^{-1}, which is lower than our experimental value (Table 4).

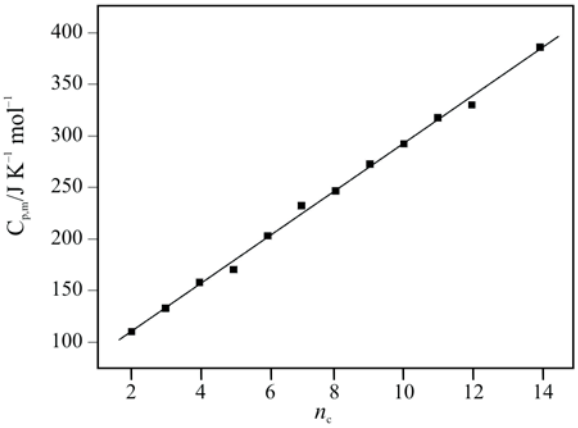

Fig. 2 The molar heat capacities $C_{p,m}$ of alkane-α,ω-diamides at T=298.15 K as a function of the number of C atoms n_C

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