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Thermodynamic properties of *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide

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Abstract

The heat capacity of *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide in both crystalline and liquid state was determined between $T = (7$ to $305)$ K and $T = (7$ to $340)$ K, respectively, by adiabatic vacuum calorimetry, generally with an uncertainty of ±0.2%. The melting temperatures and the enthalpies of fusion were measured and the entropies of fusion were estimated. The experimental data were used to calculate the standard ($p^\circ = 0.1$ MPa) thermodynamic functions of the examined amides $C^\circ_{p,\mathrm{m}}/R$, $\Delta^T_\mathrm{o} H^\circ_\mathrm{m}/R$, $\Delta^T_\mathrm{o} S^\circ_\mathrm{m}/R$, and $\Phi^\circ_\mathrm{m} = \Delta^T_\mathrm{o} S^\circ_\mathrm{m} - \Delta^T_\mathrm{o} H^\circ_\mathrm{m}/T$ (where R is the universal gas constant) in the range from $T \to 0$ to $T = 305$ (340) K.

Keywords: *N*,*N*-Dimethylformamide; *N*,*N*-Dimethylacetamide; Heat capacity; Thermodynamic functions

1. Introduction

Despite the fact that *N*,*N*-dimethylformamide (DMFA) and *N*,*N*-dimethylacetamide (DMAA) are good solvents for both electrolytes and non-electrolytes [1,2] and enjoy wide application, their thermodynamic properties have practically not been studied up to now. Only data on the heat capacity of DMFA at $T = 298.15$ K [3,4] and its enthalpy of fusion are available [5].

The goal of the present work is to measure calorimetrically the heat capacity of DMFA and DMAA in both the crystalline and liquid states between $T = (7$ and $340)$ K and to determine their thermodynamic characteristics of fusion (*i.e.* temperature, enthalpy, and entropy).

2. Experimental

The *N*,*N*-dimethylformamide (mass fraction purity 0.99 from Acros organics) was dried with phosphoric anhydride, then boiled over P_2O_5 and under flowing argon and kept over molecular sieves of analytically pure grade. The *N*,*N*-dimethylacetamide (mass fraction purity 0.999) was obtained from Aldrich and used as received. The impurity content was (0.50 ± 0.03) mol% for DMFA, as determined calorimetrically from a decrease of the melting temperature, and (0.28 ± 0.03) mol% for DMAA, as calculated by the Rossini equation [6]. The impurities were not identified and it was shown that these do not form solid solutions with the main substance.

To study the heat capacity of the tested amides from $T = (7$ to $340)$ K an automatic thermophysical device, *viz.* a BKT-3 adiabatic vacuum calorimeter, was employed [7]. The reliability of the calorimeter operation was tested by measuring the standard molar heat capacity $C^\circ_{p,\mathrm{m}}$ of standard $K - 1$ benzoic acid [8] and corundum [8] prepared at metrological institutions of the State Standard Committee of the Russian Federation. The (iron + rhodium) resistance thermometer used was calibrated on the basis of ITS-90. The calibration of the calorimeter and test results revealed that the uncertainty of heat capacity measurements at liquid helium temperatures is within 2%, which

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decreases down to 0.5% with rising temperature (up to 40 K) and becomes 0.2% in the range $T = (40$ to $340)$ K.

The molar masses of the substances studied were calculated from the IUPAC Table of Standard Atomic Weights [9].

The molar heat capacity of *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide was studied between $T = (7$ and $305)$ K and $T = (7$ and $340)$ K, respectively. The sample masses inside the calorimetric ampoule were 0.5268 g and 0.6348 g, respectively. 161 and 239 experimental $C^{\circ}_{p,\mathrm{m}}$ values, respectively, were obtained in 13 series of measurements for *N*,*N*-dimethylformamide and 45 series for *N*,*N*-dimethylacetamide (tables 1 and 2; the numbers of measurement series reflect the experimental sequence). The heat capacity of the substances in the temperature range studied amounts to (40 to 70)% of the total heat capacity of the calorimetric ampoule and the sample. The experimental $C^{\circ}_{p,\mathrm{m}}$ data were averaged by means of degree and semi-logarithmic polynomials so that the deviation of the experimental values from the corresponding smoothed $C^{\circ}_{p,\mathrm{m}} = f(T)$ curve did not exceed the measurement uncertainty. It should be noted that unlike easily crystallizing DMFA, the DMAA did not crystallize totally even on cooling it below the melting temperature by 25 K. It was necessary to cool it down to $T = 100$ K, further to heat slowly up to $T = 225$ K and afterwards the crystallization began and proceeded very slowly in the range $T = (225$ to $235)$ K and completed in about 10 days.

3. Results and discussion

3.1. Heat capacity and thermodynamic characteristics of fusion

All experimental points of the molar heat capacity (tables 1 and 2) and the averaging $C^{\circ}_{p,\mathrm{m}} = f(T)$ curves in the ranges $T = (7$ to $305)$ K and $T = (7$ to $340)$ K are illustrated in figures 1 and 2. The experimental molar heat capacity of the amides in the crystalline state gradually increases with temperature (figures 1 and 2, curves AB) until the fusion of crystals causes a steep increase of $C^{\circ}_{p,\mathrm{m}}$ (curves BC). In the liquid state, $C^{\circ}_{p,\mathrm{m}}$ increases slowly with temperature (curves EF): in the case of DMFA, it becomes higher only by 5.4% in the range $T = (213$ to $305)$ K and with DMAA by 8.3% between $T = (255$ and $340)$ K. The increase in the mass of the DMAA molecule as compared with DMFA due to the substitution of a hydrogen atom for a CH_3-group brings about the increase of the heat capacity of DMAA by (12 to 14)% in the range $T = (15$ to $210)$ K and by *ca.* 17% in the liquid state.

The procedure for the determination of the dependence of thermodynamic equilibrium triple-point temperatures

TABLE 1
Experimental molar heat capacities of *N*,*N*-dimethylformamide ($M(C_3H_7NO) = 73.0944\ \mathrm{g \cdot mol^{-1}}$; $R = 8.3144\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)

T/K	$C^{\circ}_{p,\mathrm{m}}/R$	T/K	$C^{\circ}_{p,\mathrm{m}}/R$	T/K	$C^{\circ}_{p,\mathrm{m}}/R$	T/K	$C^{\circ}_{p,\mathrm{m}}/R$	T/K	$C^{\circ}_{p,\mathrm{m}}/R$	T/K	$C^{\circ}_{p,\mathrm{m}}/R$
Series 10		20.28	1.201	79.34	6.627	155.69	10.52	206.80	43.54	236.14	17.16
7.54	0.0906	21.81	1.360	*Series 2*		158.66	10.64	211.17	385.8	239.07	17.20
8.29	0.116	24.35	1.681	82.06	6.797	161.62	10.75	213.00	17.13	*Series 5*	
9.52	0.186	26.01	1.885	84.87	6.964	164.59	10.88	*Series 8*		235.55	17.14
Series 11		28.18	2.153	87.85	7.144	167.56	11.01	215.30	17.02	238.73	17.22
7.59	0.0918	29.89	2.355	90.82	7.323	170.53	11.16	217.98	17.08	242.25	17.26
8.21	0.112	32.35	2.623	93.80	7.493	173.49	11.37	220.95	17.05	245.77	17.24
8.88	0.143	34.82	2.896	96.76	7.658	178.40	11.62	223.91	17.10	249.28	17.25
9.41	0.176	37.30	3.156	99.73	7.837	*Series 4*		226.86	17.10	252.78	17.28
9.91	0.209	39.15	3.347	102.70	8.004	184.40	11.96	229.81	17.14	256.28	17.33
10.37	0.2399	40.98	3.530	105.67	8.155	191.80	12.63	232.77	17.14	262.79	17.38
10.81	0.2722	43.45	3.763	108.64	8.321	201.10	16.78	235.72	17.18	*Series 7*	
11.24	0.3047	45.93	3.988	111.61	8.460	207.57	53.61	238.66	17.20	261.17	17.36
11.66	0.3339	*Series 12*		114.57	8.612	*Series 6*		241.60	17.21	263.79	17.37
12.07	0.3603	42.91	3.719	*Series 1*		184.65	12.17	244.54	17.24	266.68	17.42
12.44	0.3868	44.78	3.885	106.15	8.193	191.10	12.69	247.48	17.25	269.56	17.44
12.83	0.4299	49.17	4.290	109.01	8.336	198.90	14.93	250.41	17.26	272.44	17.48
13.05	0.4499	51.08	4.462	111.97	8.497	201.51	18.10	253.34	17.26	275.31	17.49
13.48	0.4831	53.56	4.687	114.94	8.630	205.99	30.04	256.26	17.31	278.16	17.51
14.16	0.5434	56.03	4.908	117.89	8.785	209.15	82.04	259.17	17.32	278.16	17.51
14.83	0.6071	58.51	5.127	120.75	8.913	211.25	424.6	262.10	17.36	281.01	17.57
15.49	0.6762	60.98	5.304	123.71	9.057	212.65	1340	265.01	17.39	283.85	17.63
16.15	0.7355	63.46	5.490	126.68	9.172	216.03	17.05	267.92	17.39	286.68	17.64
16.81	0.8061	65.93	5.674	129.64	9.320	217.78	17.04	270.82	17.42	289.51	17.68
17.45	0.8788	68.4	5.916	132.61	9.453	222.56	17.08	273.71	17.44	292.32	17.73
18.10	0.9502	70.88	6.057	138.24	9.730	225.22	17.10	276.60	17.49	*Series 13*	
18.75	1.023	73.21	6.259	146.91	10.19	228.18	17.13	279.47	17.51	298.15	17.82
19.20	1.068	75.22	6.373	149.76	10.31	231.13	17.16	*Series 3*		301.50	17.88
19.64	1.125	77.32	6.532	152.73	10.43	*Series 9*		230.54	17.14		
						200.50	15.71	233.19	17.19		