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Heat capacity and thermodynamic properties of *N*-(2-cyanoethyl) aniline ($C_9H_{10}N_2$)

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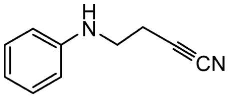
Abstract

The low temperature heat capacities of *N*-(2-cyanoethyl)aniline were measured with an automated adiabatic calorimeter over the temperature range from 83 to 353 K. The temperature corresponding to the maximum value of the apparent heat capacity in the fusion interval, molar enthalpy and entropy of fusion of this compound were determined to be 323.33 ± 0.13 K, 19.4 ± 0.1 kJ mol^{-1} and 60.1 ± 0.1 J K^{-1} mol^{-1}, respectively. Using the fractional melting technique, the purity of the sample was determined to be 99.0 mol% and the melting temperature for the tested sample and the absolutely pure compound were determined to be 323.50 and 323.99 K, respectively. A solid-to-solid phase transition occurred at 310.63 ± 0.15 K. The molar enthalpy and molar entropy of the transition were determined to be 980 ± 5 J mol^{-1} and 3.16 ± 0.02 J K^{-1} mol^{-1}, respectively. The thermodynamic functions of the compound $[H_T - H_{298.15}]$ and $[S_T - S_{298.15}]$ were calculated based on the heat capacity measurements in the temperature range of 83–353 K with an interval of 5 K.

Keywords: *N*-(2-cyanoethyl)aniline; Heat capacity; Thermodynamic properties; Adiabatic calorimetry

1. Introduction

N-(2-cyanoethyl)aniline ($C_9H_{10}N_2$, CAS: 1075-76-9) is an important raw material in the syntheses of azo dye. Its molecular structure is as follows:



Bardorff et al. ever utilized *N*-(2-cyanoethyl)aniline to prepare photographic films component [1]. Its derivative, such as *N*-2-cyanoethyl-*N*-2-hydroxy ethylaniline was used to synthesize *p*-nitro-*o*-trifluoromethyl benzene-azo-*N*-2-cyanoethyl-*N*-hydroxyalkylaniline dye compound [2]. Most of the previous works [3–5] focused on how to synthesize this substance. For example [6,7] a mixture of 12.95 g (0.10 mol) of aniline hydrochloride, 6.6 g (0.12 mol) of acrylonitrile and 9.1 g (0.12 mol) of diethylamine reacted in the round-bottomed flask at 453.15 K for 2.5 h. Through a series of treatment the product solidifies in the form of colorless plates with melting point of 321.2–324.2 K.

However, the thermodynamic properties of this substance were scarcely reported. For the application and theoretical research concerned with the substance, the thermodynamic data of this substance are urgently needed.

Heat capacity is one of the most fundamental thermodynamic properties of substances and it closely related to other physical and chemical properties. Heat capacity determinations of various compounds have attracted many researchers. Adiabatic calorimetry is one of the most accurate method for obtaining the heat capacity, melting point and enthalpy of fusion of substances. In the present paper, low temperature heat capacity measurements were carried out with an adiabatic calorimeter over the temperature range from 83 to 353 K, and thermodynamic properties such as molar enthalpies and entropies of phase transitions as well as chemical purity were determined based on the heat capacity measurements. The

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thermodynamic functions $[H_{\mathrm{T}} - H_{298.15}]$ and $[S_{\mathrm{T}} - S_{298.15}]$ were calculated from heat capacity data in the temperature range of 83–353 K.

2. Experimental

2.1. Sample

The *N*-(2-cyanoethyl)aniline is a lavender crystal. The sample used for the present calorimetric study was purchased from J&K Chemical Ltd. The labeled purity is >0.980 mass fraction. The sample was purified by re-crystallization three times using ethanol with an analytical grade prior to the calorimetric experiments. The melting point of the purified sample was determined to be $T = 322.7$–323.8 K with a microscopic melting point device (model: BY-1, Yazawa Co., Japan), which is in agreement with the value reported in literature [6,7]. Finally, the IR (model: 260-10, Hitachi Co., Japan) was employed to affirm the structure of the sample, which is identical with that given by NIST [8].

2.2. Adiabatic calorimetry

Heat capacity measurements were carried out in a high-precision automated adiabatic calorimeter described elsewhere [9]. The calorimeter mainly consisted of a sample cell, a thermometer, a heater, two adiabatic shields, two sets of chromel–copel thermocouples and a high vacuum system. The sample cell was made of gold-plated copper with internal volume of 6 cm^3. A miniature platinum resistance thermometer made by the Shanghai Institute of Industrial Automatic Meters, China, was used to measure the temperature of the calorimeter cell. The measurement resolution of platinum resistance thermometer we used is 0.001 K. The thermometer was calibrated on the basis of the ITS-90 by the Station of Low Temperature Metrology, Chinese Academy of Sciences. The thermometer was placed in the copper sheath at the bottom of the sample cell. After loading the sample into the cell, the upper cover and body of the cell were sealed with a special kind of epoxy adhesive (epoxy resin:curing agent = 5:1). The cell was evacuated to 10^{-3} Pa and then a small amount of helium gas was introduced into the cell through a copper capillary on the upper cover to promote the heat conduction within the cell. After the copper capillary was pinched off from its end, the resulted fracture was sealed with the tin solder. The cell was surrounded with two adiabatic shields. The whole calorimetric system was kept in a high vacuum with residual pressure of 10^{-3} Pa to obtain good adiabatic conditions.

Liquid nitrogen was used as the cooling medium. One set of differential thermocouples was used to detect the temperature difference between the sample cell and the inner shield. Likewise, the other set of thermocouples was installed between the inner and outer shields. The temperature difference between them was automatically kept to be about 10^{-3} K during the whole experiment. The sample cell was heated by the standard discrete heating method. The temperature increment for a heating period was 2–4 K, and temperature drift was maintained about 10^{-4} K min^{-1} during each equilibrium period. The data were automatically collected through a Data Acquisition/Switch Unit (Model: 34970A, Agilent USA) and processed on line by a personal computer according to the program developed in our thermochemistry laboratory [10].

The sample amount used for the heat capacity measurement is 2.974 g, which is equivalent to 20.343 m mol based on its molar mass of 146.19 g mol^{-1}. Prior to heat capacity measurements of the sample, the reliability of the calorimetric apparatus was verified by heat capacity measurements of the reference standard material, synthetic sapphire (α-$\mathrm{Al_2O_3}$, SRM 720). The deviation of our calibration results from the recommended values reported by Archer [11] is within ±0.5% in the temperature range from 80 to 360 K.

3. Results and discussion

3.1. Heat capacity

Experimental molar heat capacities of *N*-(2-cyanoethyl)aniline measured by the adiabatic calorimeter over the temperature range from 83 to 353 K are listed in Table 1 and plotted in Fig. 1. The C_p–T curve in Fig. 1 indicates that there is no thermal anomaly over the temperature range from 83 to 305 K, which means that this compound is stable at temperatures below 305 K.

However, two phase-transitions were observed over the temperature range from 305 to 353 K. The first transition occurred between 305 and 312 K with the peak temperature of 310.63 K. The second one took place between 312 and 325 K with the peak temperature of 323.33 K. Since the melting point of the compound is about 323 K determined

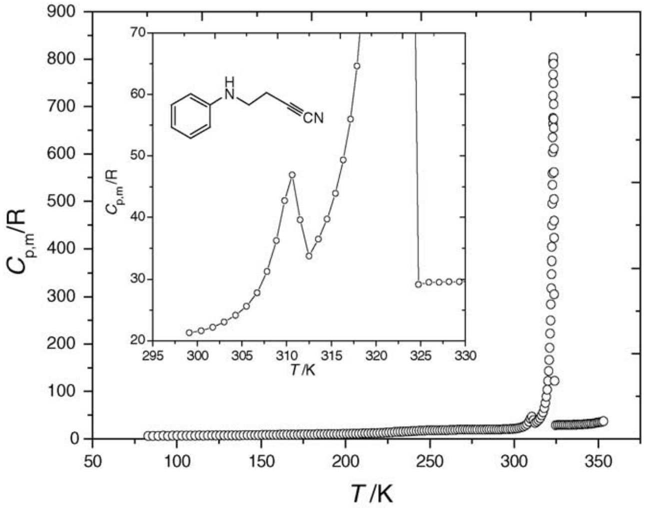

Fig. 1. Experimental molar heat capacities ($C_{p,\mathrm{m}}$) of *N*-(2-cyanoethyl)-aniline plotted against temperature.

Table 1
Experimental molar heat capacities of *N*-(2-cyanoethyl)aniline ($M = 146.19\ \mathrm{g\,mol^{-1}}$, $R = 8.314472\ \mathrm{J\,mol^{-1}\,K^{-1}}$)

T (K)	$C_{p,\mathrm{m}}/R$	T (K)	$C_{p,\mathrm{m}}/R$	T (K)	$C_{p,\mathrm{m}}/R$
83.11	6.35	225.88	13.5	317.16	56.0
85.94	6.41	227.60	14.0	317.89	64.7
88.94	6.51	229.29	14.6	318.55	75.7
91.87	6.65	230.95	14.9	319.14	88.8
94.73	6.58	232.59	15.1	319.66	104
97.54	6.65	234.22	15.5	320.12	122
100.30	6.66	235.85	15.7	320.52	143
103.01	6.73	237.47	15.9	320.86	166
105.67	6.96	239.08	16.3	321.16	192
108.29	6.99	240.67	16.8	321.42	222
110.86	7.05	242.24	17.0	321.65	245
113.39	7.18	243.78	17.3	321.85	284
115.91	7.11	245.31	17.5	322.03	318
118.39	7.20	246.85	17.6	322.19	347
120.86	7.18	248.39	17.7	322.33	375
123.29	7.24	249.91	17.8	322.45	404
125.69	7.37	251.45	17.9	322.56	450
128.08	7.36	252.99	18.0	322.66	495
130.44	7.39	254.53	18.0	322.75	535
132.78	7.46	256.06	18.1	322.83	559
135.10	7.55	257.59	18.2	322.90	604
137.39	7.63	259.11	18.4	322.97	635
139.66	7.73	260.62	18.6	323.03	663
141.91	7.82	262.12	18.8	323.09	676
144.13	8.07	263.62	19.0	323.15	723
146.35	8.05	265.10	19.0	323.20	768
148.54	8.12	266.58	19.3	323.24	792
150.73	8.20	268.05	19.3	323.29	797
152.89	8.25	269.52	19.4	323.33	803
155.03	8.37	270.98	19.4	323.37	790
157.16	8.47	272.44	19.4	323.42	750
159.28	8.62	273.90	19.5	323.46	705
161.38	8.73	275.36	19.6	323.50	674
163.47	8.78	276.81	19.6	323.55	655
165.54	8.86	278.26	19.7	323.59	611
167.59	8.94	279.70	19.7	323.64	562
169.63	9.04	281.13	19.8	323.69	505
171.66	9.14	282.56	19.8	323.73	459
173.68	9.26	283.98	19.8	323.78	423
175.70	9.36	285.41	19.9	323.83	305
177.67	9.40	286.82	19.9	324.00	122
179.65	9.49	288.23	19.9	324.78	29.1
181.61	9.61	289.63	20.0	325.93	29.5
183.57	9.77	291.02	20.0	327.07	29.5
185.51	9.82	292.39	20.1	328.20	29.6
187.45	9.87	293.74	20.3	329.34	29.6
189.37	9.98	295.08	20.5	330.46	29.7
191.29	10.1	296.42	20.6	331.59	29.7
193.19	10.1	297.76	20.9	332.72	29.7
195.09	10.2	299.09	21.3	333.84	29.7
196.97	10.2	300.41	21.6	334.96	29.8
198.84	10.4	301.72	22.2	336.08	30.1
200.68	10.6	303.00	23.1	337.19	30.2
202.52	10.6	304.27	24.2	338.30	30.4
204.36	10.9	305.50	25.6	339.40	30.5
206.19	11.1	306.69	27.8	340.50	30.7
208.02	11.2	307.82	31.3	342.69	31.2
209.84	11.4	308.85	36.2	343.77	31.5
211.66	11.6	309.78	42.7	344.84	31.9
213.46	11.7	310.63	46.9	345.90	32.3
215.26	11.9	311.50	39.6	346.95	32.8
217.05	12.1	312.51	33.7	348.01	33.4
218.84	12.3	313.55	36.5	349.04	34.1
220.61	12.6	314.54	39.7	351.08	35.4
222.38	12.9	315.48	43.9	352.08	36.1
224.14	13.4	316.35	49.3	353.07	37.2

with the microscopic melting point device, the peak temperature of the second transition agrees with this temperature. Therefore, the second transition corresponds to the fusion of *N*-(2-cyanoethyl)aniline. Hence, the first transition, probably, corresponds to a solid–solid phase transition of the substance.

It is noted from the above analysis that there are two stable phase stages and two phase-change stages in C_p–T curve, which involve a solid phase stage from 83 to 305 K, a solid–solid phase transition stage from 305 to 312 K, a solid–liquid phase transition stage from 312 to 325 K and a liquid phase stage from 325 to 353 K, respectively. The values of experimental heat capacities in the two stable phase regions can be fitted to the following polynomial equations with least square method [11].

For the solid phase over the temperature range 83–305 K:

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 84.3 + 58.7X + 129X^2 + 223X^3 - 171X^4 - 628X^5 - 15.8X^6 + 535X^7 + 103X^8 - 112X^9 \tag{1}$$

where X is the reduced temperature, $X = [(T\,(\mathrm{K})) - 194]/111$, T is the experimental temperature, 194 is obtained from polynomial $(T_{\max} + T_{\min})/2$, 111 is obtained from polynomial $(T_{\max} - T_{\min})/2$, $T_{\max}$ is the upper limit (305 K) and $T_{\min}$ is the lower limit (83 K) of the above temperature region. The correlation coefficient of the fitting $R^2 = 0.9984$.

For the liquid phase over the temperature range 325–353 K:

$$C_{p,\mathrm{m}}\,(\mathrm{J\,K^{-1}\,mol^{-1}}) = 253 + 18.6X + 22.9X^2 + 13.8X^3 \tag{2}$$

where X is the reduced temperature, $X = \{T\,(\mathrm{K}) - 339\}/14$. T is the experimental temperature, 339 is obtained from polynomial $(T_{\max} + T_{\min})/2$, 14 is obtained from polynomial $(T_{\max} - T_{\min})/2$, $T_{\max}$ is the upper limit (353 K) and $T_{\min}$ is the lower limit (325 K) of the above temperature region. The correlation coefficient of the fitting $R^2 = 0.9986$.

3.2. *The temperature, enthalpy and entropy of solid–solid phase transition and melting point, enthalpy and entropy of fusion*

Two series of heat capacity measurements in the range of phase change were made so that the phase change could be confirmed. The sample was cooled with different cooling rates (20 and 5 K min^{-1}). Similar results were obtained for the two series of measurements. The molar enthalpies of the first and second phase transitions, $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ in C_p–T curve were derived according to the following Eqs. (3) and (4):

$$\Delta_{\mathrm{trs}}H_{\mathrm{m}} = \frac{Q_1 - n\int_{T_i}^{T_{\mathrm{trs}}} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T - n\int_{T_{\mathrm{trs}}}^{T_j} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T - \int_{T_i}^{T_j} C_p(1)\,\mathrm{d}T}{n} \quad (3)$$

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}} = \frac{Q_2 - n\int_{T_i}^{T_{\mathrm{trs}}} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T - n\Delta_{\mathrm{trs}}H_{\mathrm{m}} - n\int_{T_{\mathrm{trs}}}^{T_j} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T - n\int_{T_j}^{T_{\mathrm{m}}} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T - n\int_{T_{\mathrm{m}}}^{T_{\mathrm{f}}} C_{p,\mathrm{m}}(\mathrm{l})\,\mathrm{d}T - \int_{T_i}^{T_{\mathrm{f}}} C_p(2)\,\mathrm{d}T}{n} \quad (4)$$

where T_i is a temperature slightly lower than the solid–solid transition temperature, T_j a temperature slightly higher than the solid–solid transition temperature, T_{trs} and T_{m} are solid–solid transition temperature and melting temperature, respectively. T_{f} is a temperature slightly higher than the final transition temperature, Q_1 the total energy introduced into the sample cell from T_i to T_j, Q_2 the total energy introduced into the sample cell from T_i to T_{f}, $C_p(1)$ the heat capacity of the sample cell from T_i to T_j, $C_p(2)$ the heat capacity of the sample cell from T_i to T_{f}, $C_{p,\mathrm{m}}(\mathrm{s})$ the fitted heat capacity of the sample in solid phase from T_i to T_{m}, $C_{p,\mathrm{m}}(\mathrm{l})$ the fitted heat capacity of the sample in liquid phase from T_{m} to T_{f} and n is molar amount of the sample. The heat capacity polynomials mentioned above were used to calculate the enthalpy of the phase transitions, and were numerically integrated to obtain the values of the standard thermodynamic functions relative to $T = 298.15$ K. The calculated results are listed in Table 2.

3.3. Thermodynamic functions of the substance

The thermodynamic functions of the *N*-(2-cyanoethyl)aniline relative to the reference temperature 298.15 K were calculated in the temperature range 83–305 and 325–353 K with an interval of 5 K, using the polynomial equation for heat capacity and thermodynamic relationships as follows:

- Before melting

$$H_T - H_{298.15} = \int_{298.15}^{T} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T \quad (5)$$

$$S_T - S_{298.15} = \int_{298.15}^{T} \left[\frac{C_{p,\mathrm{m}}(\mathrm{s})}{T}\right]\mathrm{d}T \quad (6)$$

- After melting

$$H_T - H_{298.15} = \int_{298.15}^{T_i} C_{p,\mathrm{m}}(\mathrm{s})\,\mathrm{d}T + \Delta_{\mathrm{trs}}H_{\mathrm{m}} + \Delta_{\mathrm{fus}}H_{\mathrm{m}} + \int_{T_{\mathrm{f}}}^{T} C_{p,\mathrm{m}}(\mathrm{l})\,\mathrm{d}T \quad (7)$$

$$S_T - S_{298.15} = \int_{298.15}^{T_i} \left[\frac{C_{p,\mathrm{m}}(\mathrm{s})}{T}\right]\mathrm{d}T + \frac{\Delta_{\mathrm{trs}}H_{\mathrm{m}}}{T_{\mathrm{trs}}} + \frac{\Delta_{\mathrm{fus}}H_{\mathrm{m}}}{T_{\mathrm{m}}} + \int_{T_{\mathrm{f}}}^{T} \left[\frac{C_{p,\mathrm{m}}(\mathrm{l})}{T}\right]\mathrm{d}T \quad (8)$$

in which T_i is the temperature at which the solid–solid phase transition started; T_{f} is the temperature at which the melting ended; $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ is the molar enthalpy of solid–solid phase transition; $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ is the molar enthalpy of fusion; T_{trs} is the temperature of solid–solid phase transition; T_{m} is the melting temperature; $C_{p,\mathrm{m}}(\mathrm{s})$ and $C_{p,\mathrm{m}}(\mathrm{l})$ is the fitted heat capacity of the substance in solid and liquid state, respectively.

The thermodynamic functions, $H_{\mathrm{T}} - H_{298.15}$, $S_{\mathrm{T}} - S_{298.15}$, are listed in Tables 3 and 4, respectively.

Table 2
Thermodynamic parameters of *N*-(2-cyanoethyl)aniline gained from heat capacity measurements

Thermodynamic parameters	Series 1	Series 2	Mean value
T_{trs} (K)	310.77	310.48	310.63
T_{m} (K)	323.47	323.20	323.33
$\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ (J mol^{-1})	985	975	980
$\Delta_{\mathrm{trs}}S_{\mathrm{m}}$ (J K^{-1} mol^{-1})	3.17	3.14	3.16
$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ (kJ mol^{-1})	19.5	19.4	19.4
$\Delta_{\mathrm{fus}}S_{\mathrm{m}}$ (J K^{-1} mol^{-1})	60.2	60.1	60.1

3.4. Purity determination of the sample

Adiabatic calorimetry provides an accurate way for determining the purity of a substance. Here, we suppose that the impurity resolves ideally in the liquid phase of the sample and does not resolve at all in the solid phase. The total amount of impurities does not exceed a couple of mol%. According to the ideal solution law, the relation between the mole fraction N ($N \ll 1$) of a small amount of impurities in the sample and its melting-point depression is as follows:

$$N = \frac{\Delta H_{\mathrm{m}}(T_0 - T_1)}{RT_0^2} \quad (9)$$

where T_0 is the melting point of an absolutely pure substance; T_1 the melting point of the given sample, ΔH_{m} the heat of fusion of the sample and R is molar gas constant. As for the liquid solution formed by a part of the sample melted, given that N' is the mole fraction of the impurities and T is the melting point of the solution, then

$$N' = \frac{\Delta H_{\mathrm{m}}(T_0 - T)}{RT_0^2} \quad (10)$$

If it is assumed that the impurities are solid-insoluble and all of the impurities are transferred completely into the liq-

Table 3
Calculated thermodynamic functions of *N*-(2-cyanoethyl)aniline in the solid phase

T	$C_{p,\mathrm{m}}/R$	$[(H_\mathrm{T}-H_{298.15})/R]$ $(\times10^{-3}\ \mathrm{K})$	$(S_\mathrm{T}-S_{298.15})/R$
83	6.33	−2.57	−13.3
88	6.47	−2.54	−13.0
93	6.62	−2.51	−12.6
98	6.74	−2.47	−12.2
103	6.85	−2.44	−11.9
108	6.93	−2.41	−11.6
113	7.02	−2.37	−11.3
118	7.11	−2.34	−11.0
123	7.23	−2.30	−10.7
128	7.37	−2.26	−10.4
133	7.53	−2.23	−10.1
138	7.73	−2.19	−9.80
143	7.94	−2.15	−9.52
148	8.15	−2.11	−9.24
153	8.37	−2.07	−8.97
158	8.58	−2.03	−8.70
163	8.79	−1.98	−8.43
168	8.98	−1.94	−8.16
173	9.17	−1.89	−7.89
178	9.36	−1.85	−7.63
183	9.56	−1.80	−7.37
188	9.80	−1.75	−7.10
193	10.1	−1.70	−6.84
198	10.4	−1.65	−6.58
203	10.8	−1.60	−6.32
208	11.3	−1.54	−6.05
213	11.9	−1.48	−5.77
218	12.6	−1.42	−5.49
223	13.3	−1.36	−5.19
228	14.2	−1.29	−4.89
233	15.0	−1.22	−4.57
238	15.9	−1.14	−4.25
243	16.7	−1.06	−3.91
248	17.5	−0.970	−3.56
253	18.2	−0.881	−3.20
258	18.8	−0.789	−2.84
263	19.2	−0.694	−2.47
268	19.4	−0.597	−2.11
273	19.5	−0.500	−1.75
278	19.5	−0.402	−1.40
283	19.5	−0.305	−1.05
288	19.7	−0.207	−0.705
293	20.2	−0.107	−0.362
298.15	21.5	0.000	0.000
303	23.6	0.109	0.362
305	24.8	0.157	0.520

Table 4
Calculated thermodynamic functions of *N*-(2-cyanoethyl)aniline in the liquid phase

T	$C_{p,\mathrm{m}}/R$	$[(H_\mathrm{T}-H_{298.15})/R]$ $(\times10^{-3}\ \mathrm{K})$	$(S_\mathrm{T}-S_{298.15})/R$
325	29.3	2.62	8.15
330	29.7	2.77	8.60
335	29.9	2.92	9.05
340	30.6	3.07	9.50
345	32.0	3.22	9.95
350	34.6	3.39	10.4
353	37.0	3.50	10.7

Table 5
Experimental values of melted fraction (F) and equilibrium temperature (T) of *N*-(2-cyanoethyl)aniline

$F=q/Q$	$1/F$	T (K)
0.223	4.48	321.85
0.271	3.70	322.19
0.320	3.12	322.45
0.371	2.70	322.66
0.423	2.36	322.83
0.476	2.09	322.97
0.530	1.89	323.09
0.584	1.71	323.20

uid phase when the melting started, the relative amount of the sample in the liquid phase will be increasingly more in the process of the melting; on the other hand, since the total amount of the impurities remains constant, the mole fraction of the impurities in the liquid phase will gradually decrease. Given: F is the ratio of the amount of the sample in the liquid phase to the total amount of the sample, then

$$F=\frac{q}{Q} \tag{11}$$

where F is also designated as the fraction melted, its value being the ratio of the heat required to melt a part of the sample (q) to the total heat required to melt the whole sample (Q). Obviously, F is inversely proportional to the mole fraction of the impurities in the liquid phase, that is,

$$N'=\frac{1}{F}N \tag{12}$$

Substituting Eqs. (9) and (10) into Eq. (12), we have

$$T_0-T=\frac{1}{F}(T_0-T_1) \tag{13}$$

From (13) it may be observed that the relation between the melting point, or the equilibrium melting temperature T and

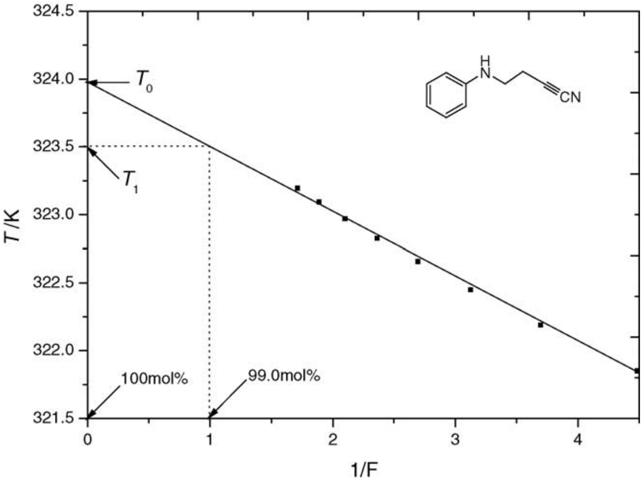

Fig. 2. The melting curve of *N*-(2-cyanoethyl)aniline with temperature plotted against reciprocal of the melting fraction (T_0 = 323.99 K, T_1 = 323.50 K).

$1/F$ is linear. The purity of the sample was determined by a set of equilibrium melting temperatures (T) and melting fractions (F) corresponding to these temperatures [12–14]. The calculated results are shown in Table 5. A plot of the equilibrium melting temperature (T) versus the reciprocal of the melting fractions ($1/F$) is a straight line, as shown in Fig. 2. The T_0 is the temperature when $1/F$ is 0 and T_1 is the temperature when $1/F$ equals to 1. From Fig. 2, the $T_0 = 323.99$ K and $T_1 = 323.50$ K were obtained, respectively. Thus, we calculated the mol percentage of impurities, $N = 0.010$ mole fraction from Eq. (9), and the purity of the sample amounted to $1 - N = 0.990$ mole fraction.

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