# Heat capacities of urea, N-methylurea, N-ethylurea, N-(n)propylurea, and N-(n)butylurea in the range 200 to 360 K [☆]

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## Abstract

The heat capacities at constant pressure of urea, N-methylurea, N-ethylurea, N-(n)propylurea and N-(n)butylurea were measured by differential scanning calorimetry over the range 200–360 K, in gas-flow conditions. A He + Ne mixture and $N_2$ only were selected as the purge gases below and above room temperature, respectively. Benzoic acid was used as the reference material and the accuracy of the measurements was estimated to be within 2% across the temperature range. The heat capacities at 298.15 K were obtained by interpolating the smoothed fitting equations.

No anomalies were detected for urea or N-methylurea. One fully reversible solid–solid transition was observed for N-ethylurea at $T = (294.5 \pm 2.0)$ K, with $\Delta_{trs}H_m = (1.0 \pm 0.3)$ kJ mol$^{-1}$, and for N-(n)propylurea at $T = (289.6 \pm 1.0)$ K, with $\Delta_{trs}H_m = (3.0 \pm 0.2)$ kJ mol$^{-1}$. Two solid–solid transitions were found for N-(n)butylurea at $T = (315.0 \pm 2.0)$ K, with $\Delta_{trs}H_m = (7.0 \pm 2.0)$ kJ mol$^{-1}$ and at $T = (346.0 \pm 1.2)$ K, with $\Delta_{trs}H_m = (1.0 \pm 0.1)$ kJ mol$^{-1}$, the first one being recoverable at temperatures lower than 240 K only.

Keywords: DSC; Heat capacity; N-(mono)alkylureas; Phase transitions; Urea

## 1. Introduction

The interest in "model compounds" in the study of the physicochemical properties of biological systems, as well as in polymer science, is well known. Urea and related

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substances, such as its N-alkyl derivatives, can be considered as simple model compounds that exhibit strongly opposite features (hydrophilic and hydrophobic) and show to a varying extent the characteristic property of denaturing proteins in water solution. Therefore, in recent years a number of works have been devoted to collecting thermodynamic data on this class of substances, either in solution or as pure, generally solid, compounds.

Enthalpies of fusion [1], enthalpies of sublimation [2–4], enthalpies of formation [5], and enthalpies of solution at infinite dilution [6–8] of urea and various alkylureas have been reported. Moreover, some series of heat capacity measurements on urea are also available [9–13]. However, no data concerning alkylureas have yet been published, except those on N-methylurea in a recent paper [14]. However, we were informed by these authors that new experimental data obtained by adiabatic calorimetry and concerning a number of N-alkylureas are in the course of publication [15, 16].

The heat capacities of the pure substances can be used to derive enthalpy and entropy changes at 298.15 K from both sublimation and vaporisation experimental data, as well as to calculate their partial molar heat capacities as solutes at infinite dilution. This is the basic reason why the determination of the heat capacities of urea and related alkyl compounds has been undertaken in our laboratories.

The aim of the present paper is to measure by differential scanning calorimetry (DSC) the molar heat capacities of urea and some of its monosubstituted N-alkyl derivatives over the temperature range 200–360 K, i.e. somewhat below their melting temperatures. Furthermore, a more general purpose of this work is to confirm the validity of the DSC technique as a general tool for $C_p$ measurements, especially when only very small amounts of purified materials, e.g. those extracted from biological samples, are available. The presence in the literature of some series of $C_{p,m}$ values for urea, which were measured mainly by adiabatic calorimetry in different laboratories, has given us the opportunity of testing the precision and reliability of our data and, more generally, checking the applicability of our DSC equipment and technique to accurate heat capacity determinations, in particular with organic compounds.

## 2. Experimental

### 2.1. Materials

The reference material used in the heat capacity calibration procedure was benzoic acid (NPL-SRM M16-06, 99.99% mole fraction).

The products used were analytical grade reagents of different origins, as reported in Table 1. They were further purified by means of several crystallisation cycles with Fluka puriss., absol., > 99.5% ethylacetate, over molecular sieves. After being dried in vacuo at room temperature overnight and then at 343 K for 3–4 h in a Heraeus vacuum furnace, the samples obtained in the form of small flakes were stored in a desiccator. Small quantities (2–10 mg) of the products purified by recrystallisation and some only as-received, but dried at 343 K as above, were submitted to DSC runs in a high-purity (> 99.999%) $N_2$ flowing atmosphere from about 200 K up to fusion in order to: (i)

Table 1
List of the examined compounds, their commercial origin and purity, and final purity determined in this work

| Compound | Origin | Purity % (comm.) | Number of crystallisations | Purity % (DSC analysis) |
|---|---|---|---|---|
| Urea | Aldrich | 99 | 5 | 99.94[a] |
| (NH$_2$CONH$_2$) | Fluka MicroSelect | >99.5 | – | 99.97 |
| $M = 60.06\,\mathrm{g\,mol^{-1}}$ | | | 2 | 99.98 |
| | | | 4 | 99.98[a] |
| N-methylurea | EGA-Chemie | 99 | 5 | 99.96[a] |
| (CH$_3$NHCONH$_2$) | K & K | n.i. | – | 99.70 |
| $M = 74.08\,\mathrm{g\,mol^{-1}}$ | | | 3 | 99.95 |
| | | | 5 | 99.98[a] |
| N-ethylurea | EGA-Chemie | 97 | 5 | 99.89[a] |
| (C$_2$H$_5$NHCONH$_2$) | K & K | n.i. | – | 98.58 |
| $M = 88.11\,\mathrm{g\,mol^{-1}}$ | | | 2 | 99.24 |
| | | | 5 | 99.99[a] |
| N-(n)propylurea | Alfa | n.i. | – | 99.56 |
| (C$_3$H$_7$NHCONH$_2$) | Kodak | n.i. | 2 | 99.96[a] |
| $M = 102.14\,\mathrm{g\,mol^{-1}}$ | | | 5 | 99.99[a] |
| N-(n)butylurea | EGA-Chemie | 99 | 5 | 99.97[a] |
| (C$_4$H$_9$NHCONH$_2$) | Fluka puriss. | >99 | – | 99.96 |
| $M = 116.16\,\mathrm{g\,mol^{-1}}$ | | | 2 | 99.99[a] |

Key: n.i. not indicated by the supplier.
[a] Sample selected for $C_p$ measurements.

detect solid–solid phase transitions, and (ii) check their purity with the well-known method of the van't Hoff equation [17, 18] through analysis of the fusion peak profile. Since it is known that urea and N-alkylureas tend to decompose near their melting temperature, only fusion DSC scans on fresh samples were taken into account for their purity analysis. Results concerning the purity of these products (precision $\pm 0.01\%$), both as-received and after purification, are presented in Table 1, together with an indication of the samples selected for the present research.

2.2. Differential scanning calorimetry

Measurements were carried out with a Perkin-Elmer DSC-2 instrument, which was calibrated for both temperature and enthalpy in the superambient and subambient temperature ranges as previously reported [19, 20]. The uncertainty of the temperature measurements at the adopted scan speed of $0.167\,\mathrm{K\,s^{-1}}$ was within $\pm 0.2\,\mathrm{K}$.

Heat capacity measurements by DSC require calibration of the proper calorimetric signal including: (i) selection of a suitable calibrant material; (ii) adoption of an appropriate purge gas (or gas mixture), which is particularly important at subambient temperatures; and (iii) achievement of a compromise between scanning rate, sample mass and sensitivity ranges to obtain a sufficiently large signal/noise ratio.

The selection of a heat-capacity reference material suitable for DSC measurements with organic compounds, especially at low temperatures, is controversial. In this work, the relatively large amount of literature data [9–13] concerning the $C_{p,m}$ values of urea measured by adiabatic calorimetry provided a valuable check on our choice for the calibrant, as well as for the other experimental conditions. Actually, the results obtained using the synthetic sapphire provided by Perkin-Elmer, and suggested by ASTM Standards [21], were remarkably lower (by ~ 6%) than the average of the literature data. By contrast, when benzoic acid was used as the reference substance, the heat capacities of our sample of urea were in excellent agreement with the average literature data, as illustrated in Fig. 1, provided that other conditions had correctly been selected.

Therefore, benzoic acid was prepared as pressed pellets following the procedure described below and was used as the calorimetric standard across the mentioned temperature range. The experimental heat capacity values for benzoic acid determined by adiabatic calorimetry by Arvidsson et al. [22] were chosen as the reference values.

Moreover, in order to obtain reliable and reproducible heat capacity data, in particular in the temperature range between 273 and 323 K, i.e. in the region where a satisfactory overlap of DSC signal relevant to the subambient and superambient scanning should be achieved, a mixture of 10% He and 90% Ne (purity 99.9995% and > 99.98%, respectively) supplied by SIAD (Dalmine, Bergamo, Italy) was selected as the thermal exchange gas below room temperature, as suggested by Mraw and Naas
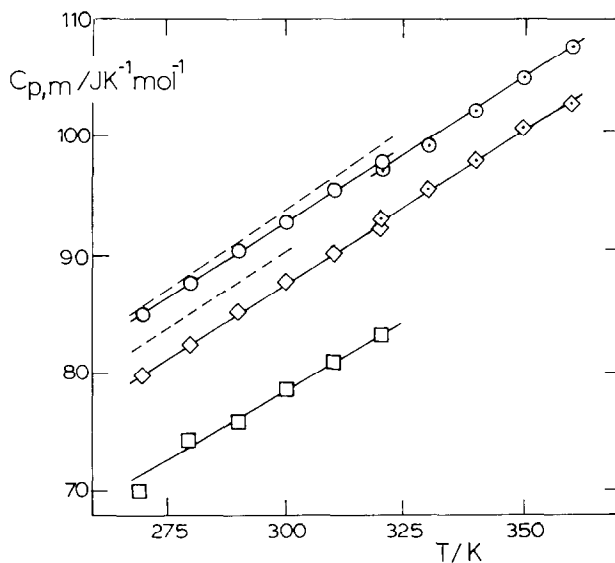


Fig. 1. Heat capacities of a single sample of urea obtained through different DSC calibration procedures concerning both the reference material and purge gas: □, sapphire, helium; ○, sapphire, (0.10 He + 0.90 Ne) mixture; ◇, sapphire, $N_2$; ○, benzoic acid, (0.10 He + 0.90 Ne) mixture; ⊙, benzoic acid, $N_2$. Dashed lines refer to selected literature values measured by adiabatic calorimetry taken from Refs. [9] (upper line) and [10] (lower line).

[23]. The low-temperature heat capacity curves recorded in the presence of this gas mixture overlapped well with those recorded with $N_2$ (purity $> 99.999\%$) as the purge gas above room temperature.

A sufficiently large signal/noise ratio in heat capacity determinations with DSC, especially at low temperatures, depends directly on the mass of sample loaded. In our case, the limiting factors were: (i) the volume of the volatile sample pan supplied by Perkin-Elmer, and (ii) the fact that both original and purified products were very low density and quite hygroscopic samples. Thus, the light powdery crystals were ground rapidly and the samples for measurements were prepared in the form of pellets (approx. 1 mm thick and 4 mm in diameter) at a pressure of $50\text{--}100\,\text{kg}\,\text{cm}^{-2}$. They were then stored for 20–30 days over $P_2O_5$ in a vacuum desiccator at room temperature, and finally sealed in Al volatile-sample pans. Therefore, the masses of the pellets employed were in the range 10–30 mg.

For urea and N-methylurea, six samples from two different products were used. Four samples were selected for N-ethyl- and N-propylurea, and three samples for N-butylurea, each alkylurea being taken from two different products, see Table 1.

No significant deviations being found among the series of data for samples from different sources, the results reported represent the average of the values collected on all the samples submitted to DSC measurements in different chronological series.

The ordinate-displacement method was adopted, covering a temperature range of 40–50 K for each run. Three reference samples and the empty sample holder were usually scanned before and after recording the series of runs necessary to explore the full temperature range of each sample of the studied compounds. The average value of the ordinate displacements in two or three subsequent runs was determined for each sample at the selected temperatures. For the reference samples and empty holder, the average of all the recorded values was taken into account.

## 3. Results and discussion

The experimental molar heat capacities at intervals of five degrees from 200 to 360 K for urea and the four N-(mono)alkylureas are reported in Table 2. These data are also plotted as a function of temperature in Fig. 2 for comparison with the literature data. It will be seen that no anomalies appear in the curves of urea and N-methylurea, whereas for the other N-alkylureas, solid–solid transitions were revealed. The discrepancy with the results in Ref. [1], where no solid phase changes were observed for N-ethylurea and N-(n)propylurea, is due to the fact that in that work no scannings were made below room temperature.

The percentage deviations of the experimental data from the smooth curve was within $\pm 2\%$ for urea and N-(n)propylurea, $\pm 2.5\%$ for N-methylurea, and $\pm 3\%$ for N-ethylurea across the experimental temperature range.

For urea, the fitting linear equation is $C_{p,\text{m}}/(\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) = (16.45 \pm 0.54) + (0.250 \pm 0.002)\,(T/\text{K})$. In Fig. 2 (curve a), our data show the same slope as those of the literature. In particular, they are slightly lower (by $\sim 1\%$) than the adiabatic calorimetry values reported in Refs. [9, 11, 13], but, for simplicity, only those of Ref. [9] are

Table 2
Experimental molar heat capacities $C_{p,m}/(\text{J K}^{-1}\text{mol}^{-1})$ at selected temperatures

| $T/K$ | Urea | $N$-methylurea | $N$-ethylurea | $N$-($n$)propylurea | $N$-($n$)butylurea |
|-----|--------|--------|--------|--------|--------|
| 200 | 66.28 | 86.16 | 100.82 | 124.89 | |
| 205 | 67.31 | 87.61 | 103.06 | 127.69 | |
| 210 | 68.85 | 88.91 | 105.26 | 131.06 | |
| 215 | 70.02 | 90.14 | 107.56 | 134.36 | |
| 220 | 71.37 | 91.28 | 109.78 | 137.61 | |
| 225 | 72.72 | 92.45 | 112.40 | 141.31 | |
| 230 | 73.96 | 93.28 | 114.63 | 145.20 | |
| 235 | 75.37 | 95.03 | 117.35 | 149.38 | |
| 240 | 76.73 | 95.84 | 119.79 | 153.61 | |
| 245 | 78.14 | 97.09 | 122.91 | 158.48 | |
| 250 | 79.26 | 98.46 | 125.70 | 164.09 | |
| 255 | 80.69 | 99.70 | 129.06 | 170.00 | |
| 260 | 81.99 | 101.19 | 132.22 | 176.27 | 178.20 |
| 265 | 83.12 | 102.41 | 135.84 | 184.83 | 183.15 |
| 270 | 84.32 | 103.97 | 138.97 | 192.54 | 187.52 |
| 275 | 85.71 | 105.32 | 143.35 | 204.71 | 192.44 |
| 280 | 87.01 | 106.76 | 148.08 | – | 195.91 |
| 285 | 87.71 | 108.41 | 153.34 | – | 197.12 |
| 290 | 89.17 | 109.72 | 160.00 | – | 199.59 |
| 295 | 90.37 | 111.09 | 167.41 | – | 203.92 |
| 300 | 91.27 | 112.86 | 175.13 | 197.39 | 210.22 |
| 305 | 92.75 | 114.09 | 184.49 | 198.89 | 213.44 |
| 310 | 94.15 | 115.68 | 194.22 | 201.90 | 217.43 |
| 315 | 95.34 | 117.03 | 202.43 | 204.90 | – |
| 320 | 96.49 | 118.45 | 207.99 | 206.57 | 222.55 |
| 325 | 97.51 | 119.49 | 209.94 | 209.28 | 224.60 |
| 330 | 98.65 | 120.78 | 207.49 | 211.19 | 228.44 |
| 335 | 100.22 | 122.68 | 201.88 | 212.70 | 231.57 |
| 340 | 101.42 | 124.24 | 196.02 | 215.40 | 235.92 |
| 345 | 102.76 | 125.61 | 191.24 | 216.68 | – |
| 350 | 104.04 | 127.43 | 187.04 | 218.38 | 242.36 |
| 355 | 105.52 | | 184.53 | 220.65 | 241.68 |
| 360 | 106.74 | | 183.22 | 222.55 | 243.59 |

represented in the figure because all these data are practically coincident. The values taken from Ref. [12], which were obtained by means of a standard Calvet micro-calorimeter, although more scattered, are distributed over a similar slope and position. Another series of data obtained by adiabatic calorimetry [10] is systematically lower, even though the observed slope is maintained. Compared with the average adiabatic calorimetry data, the results of the present work are slightly lower by about 0.7% across the temperature range.

For $N$-methylurea, the fitting equation is $C_{p,m}/(\text{J K}^{-1}\text{mol}^{-1}) = (30.57 \pm 0.59) + (0.274 \pm 0.002)\,(T/K)$. In Fig. 2 (curve b), a remarkable agreement in the temperature range 200–300 K between our data and those measured by adiabatic calorimetry by

Kozyro et al. [14] is observed. However, above 300 K, the literature series progressively departs from our linear fitting.

A good agreement between our results for $N$-ethylurea and those of Ref. [15] in the range 200–260 K is illustrated in Fig. 2 (curve c). At higher temperatures, a smooth solid–solid transition, covering a relatively large interval of temperature, has been revealed by DSC measurements at various scan rates. This experimental feature is well reproducible and does not display any hysteresis on cooling. The heat capacity value at 298.15 K was evaluated from the baseline drawn on the figure.

A much sharper solid–solid transition, very probably first-order, was found in the thermal behaviour of $N$-($n$)propylurea, as shown in Fig. 2 (curve d). The present DSC results can be compared with very recent measurements by adiabatic calorimetry [16]. An excellent agreement exists in the range 200–280 K, whereas our data are slightly higher above room temperature. The heat capacity value at 298.15 K was taken by
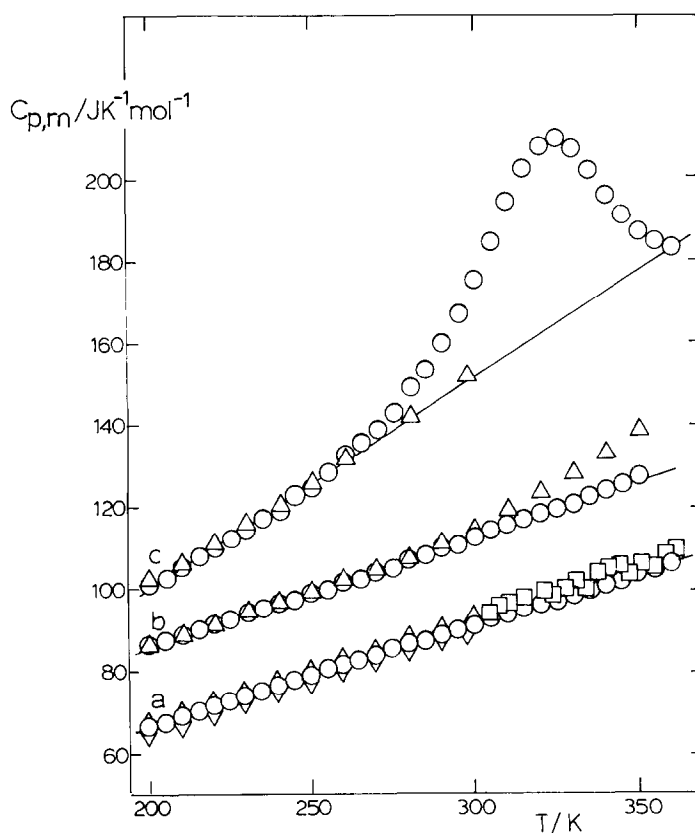


Fig. 2. Heat capacities (○, experimental and —, smoothed data) from this work compared with those of the literature. Curve a, urea: △, Ruerwhein and Huffman [9]; ▽, Sasaski and Yokotake [10]; □, Gambino and Bros [12]. Curve b, $N$-methylurea: △, Kozyro et al. [14]. Curve c, $N$-ethylurea: △, Kabo et al. [15]. Curve d, $N$-($n$)propylurea: △, Ogita et al. [16]. Curve e, $N$-($n$)butylurea: △, Kabo et al. [15].
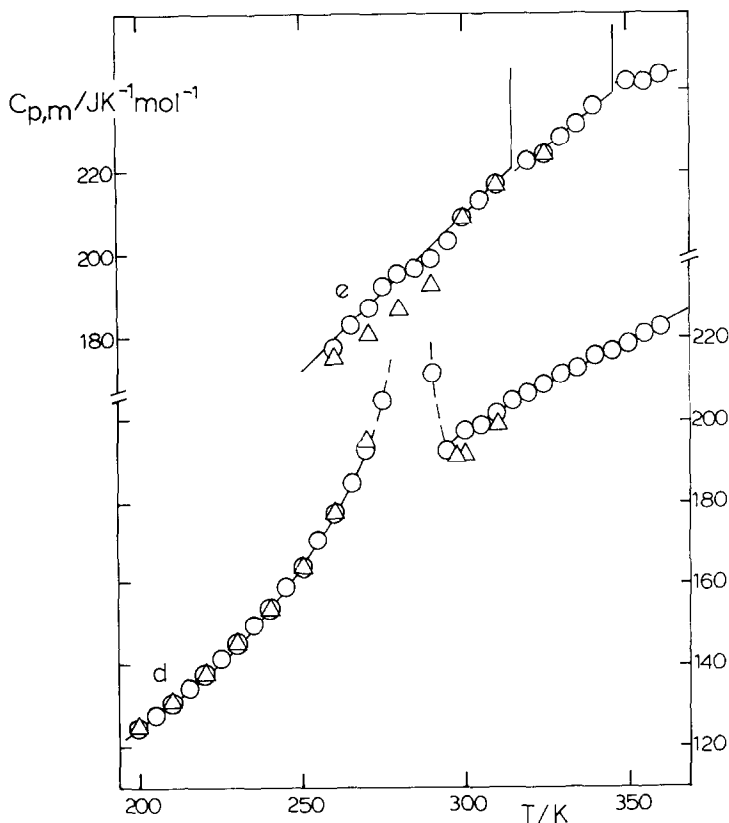
Fig. 2    (Continued)

extrapolation to this temperature of the second branch of the curve, and is about 3%
higher than that given in Ref. [16].

For N-(n)butylurea, the thermal phenomena occurring over the examined tempera-
ture range are more complicated. Two solid–solid transitions are observed (Fig. 2,
curve e), which are in agreement with data in Refs. [1, 15]. The transition at 346 K is
easily reproducible, both upon heating and cooling with slow and fast scan rates. By
contrast, the transition at 315 K displays a significant hysteresis on cooling. Actually,
this always appears with samples (purified or as-received) kept at room temperature,
but can be recorded in further heating runs only if the sample has been previously
cooled down to temperatures lower than 240 K. However, after this cooling procedure,
the same solid–solid transition was found at 296 K. As far as the heat capacity data are
concerned, our results are in good accord with those tabulated in Ref. [15].

In Table 3, our heat capacity values at 298.15 K are compared with the literature
data, including those in the course of publication. A comparison is also made with data
calculated on the basis of a recent group-additivity scheme [24]. In Table 4, the tem-
peratures and enthalpies associated with both solid–solid transitions and fusion are
summarised, showing an excellent accord with those of the literature [1, 15].

Table 3
Molar heat capacities $C_{p,m}/(J K^{-1} mol^{-1})$ at 298.15 K compared with values from the literature and calculated by a group-additivity scheme

| Compound | This work | Literature | Calculated [24] |
|---|---|---|---|
| Urea | 91.02 | 93.14 [9], 89.96 [10], 93.08 [11], 92.79 [13] | 93.00 |
| N-methylurea | 112.06 | 114.74 [14] | 139.95 |
| N-ethylurea | 150.76 | 152 [15] | 161.87 |
| N-(n)propylurea | 197.21 | 191.23 [16] | 183.79 |
| N-(n)butylurea | 207.94 | 207.9 [15] | 205.71 |

Table 4
Temperatures and enthalpies of solid–solid transition and fusion for urea and monoalkylureas

| Compound | $T_{trs}/K$ | $\Delta_{trs}H_m/(kJ mol^{-1})$ | $T_{fus}/K$ | $\Delta_{fus}H_m/(kJ mol^{-1})$ |
|---|---|---|---|---|
| Urea | | | $407.9 \pm 0.2$ | $15.03 \pm 0.12$ |
| N-methylurea | | | $375.0 \pm 0.2$ | $16.58 \pm 0.05$ |
| N-ethylurea | $294.5 \pm 2.0$ | $1.0 \pm 0.3$ | $368.9 \pm 0.5$ | $14.65 \pm 0.40$ |
| N-(n)propylurea | $289.6 \pm 1.0$ | $3.0 \pm 0.2$ | $382.0 \pm 0.5$ | $14.92 \pm 0.40$ |
| N-(n)butylurea | $315.0 \pm 2.0$ | $7.0 \pm 2.0$ | $370.0 \pm 0.3$ | $15.70 \pm 0.70$ |
| | $346.0 \pm 1.2$ | $1.0 \pm 0.1$ | | |

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