On the Thermal Stability of Urea Complexes with Organic Substances

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Urea forms crystalline complexes with almost all types of straight-chain organic compounds—hydrocarbons, ethers, aldehydes, acids, alcohols, etc. ([1,2]).

Among researchers who have dealt with questions of the formation and stability of urea complexes with organic substances, the opinion has become established that urea complexes cannot exist above its melting temperature, 132.7° ([3–6]). Although up to the present time no urea complexes stable above 132.7° have been found, nevertheless, from the thermodynamic point of view it is completely unclear why the melting temperature of urea should be the upper limit for the existence of a complex. At temperatures below 132.7° there are complexes in equilibrium with urea in its unsaturated solutions, for example aqueous ones ([7]). Urea in its unsaturated solutions, especially aqueous solutions, which are close to ideal solutions, should legitimately be regarded from the thermodynamic point of view as liquid urea with an activity lower than the activity of solid urea at the same temperature.

The thermal stability of a complex is the higher, the longer the chain of the organic compound ([2,7]). The thermal stability of a complex obtained from a mixture of organic substances is higher than the thermal stability of complexes obtained from the individual compounds entering into the mixture ([7]). Therefore, in searching for complexes stable above the melting temperature of urea, the authors carried out experiments with paraffin and ceresin, i.e., multicomponent mixtures consisting mainly of hydrocarbons of the paraffin series with long chains.

For the experiments, chemically pure urea, commercially available paraffin with molecular weight 307 and m.p. 41–43°, and purified ceresins of various grades were used. Synthetic ceresin had m.p. 82–84°.

The urea complex with ceresin or paraffin was synthesized in a sealed glass tube with a capacity of 1.5–2.5 cm^3. Formation of the urea complex with paraffin and ceresin begins only at temperatures above the melting temperature of paraffin (ceresin). The reaction between urea and ceresin proceeds very slowly—over several hours. The most favorable condition for formation of the complex is slow cooling of the molten mixture of urea with ceresin.

Figure 1

Figure 1: Figure 1

The glass tube with the complex was fastened to a rotating frame in an air thermostat with observation windows ([8]). With a slow rise of the temperature in the thermostat, the temperature of complete disappearance of the complex was determined visually:

Organic component	Temperature, °C
Paraffin	124.5
Ceresin from the Surakhany deposit	134.0
» from the Shor-Su deposit	135.0
» from the Borislav deposit	137.5
» synthetic No. 1	140.0
» synthetic No. 2	140.5
» synthetic No. 3	141.0

Urea complexes with ceresins of various grades are stable above the melting temperature of urea. The urea complex with synthetic ceresin No. 3 exists up to a temperature of 141.0°.

To verify the stability of the equilibrium between the complex and molten urea, a sealed tube containing the complex of urea with synthetic ceresine No. 3 was rotated in an air thermostat for ten hours at 136°. The complex did not decompose, and the characteristic precipitate of the complex floated in the melt of urea and ceresine. In a control sealed tube containing only urea, there was a completely transparent melt of urea.

The stability of the complex at temperatures above the melting point of urea can also be proved by another method: by studying the equilibrium between the complex and urea in its unsaturated solutions.

Fig. 1. Thermal stability of urea complexes with cetane, paraffin, and ceresine in liquid-ammonia solutions:
1 —solubility of urea in liquid ammonia, **2** —urea complex with cetane, **3** —urea complex with paraffin, **4** —urea complex with ceresine

It is known that in aqueous solutions of urea the thermal stability of the complex depends on the concentration of urea in the solution ([7]). Obviously, the curve of the temperature stability of the complex begins at a temperature below the melting point of urea and ends at a temperature above which the complex can no longer exist, already independently of the concentration of urea in the solution. Therefore, in order to judge whether the complex is stable above the melting point of urea, it is necessary to follow the course of the temperature curve. Water, as a solvent for urea, is unsuitable for these experiments, since above

100° the reaction forming ammonia and carbon dioxide from urea and water proceeds at a noticeable rate ([9]). Liquid ammonia was chosen as the solvent.

The authors measured the solubility of urea in liquid ammonia by the synthetic method of Alekseev ([10]) and obtained good agreement with the literature data ([11]) (Fig. 1). The solubility curve of urea in liquid ammonia at 46°—the melting point of the compound $CO(NH_2)_2 \cdot NH_3$—has a break.

As in experiments without solvent, the complex was synthesized in a sealed thick-walled glass tube; the tube was rotated in a thermostat, and, with a slow rise in temperature, the temperature of complete disappearance of the complex was determined visually (Fig. 1).

The curve of the temperature stability of the urea complex with paraffin ends at 124.5°, but the temperature curve of the urea complex with ceresine clearly passes above the melting point of urea and is directed toward the previously determined temperature of 141.0° (see above).

To check the correctness of the method employed, the authors investigated the thermal stability of the urea complex with cetane in aqueous urea solutions (Fig. 2) and obtained good agreement with the literature data ([7]). The curve of the temperature stability of the complex intersects the solubility curve of urea in water at 96° (Fig. 2).

In studying the thermal stability of the urea complex with cetane in ammonia solutions of urea, we found that the solubility curve of urea in liquid ammonia intersects the curve of the thermal stability of the complex at a somewhat higher temperature, namely 99° (see Fig. 1). This discrepancy can be explained by partial decomposition of urea in aqueous solutions during prolonged experiments (several—

for hours), because of which the actual concentration of urea in the aqueous solution was somewhat lower than the specified one.

The curve of the thermal stability of the urea complex with cetane intersects both branches of the solubility curve of urea in liquid ammonia (see Fig. 1), and the complex is stable within the temperature interval.

When experiments were carried out to measure the thermal stability of the complexes, some qualitative observations were made on the conditions for complex formation.

If, in experiments with unsaturated solutions of urea in liquid ammonia, the temperature at which the urea complex with cetane (paraffin, ceresin) is completely destroyed is reached, then upon lowering the temperature by 5-10° the complex does not form again, even when the tube is rotated for many hours in the thermostat. For the complex to form, cooling by 15-25° is necessary, and in some experiments even by 40-45°. If, when the temperature is raised, the complex is not destroyed completely, but a small "seed" is left, then when the temperature is lowered the amount of complex does not increase during rotation

Fig. 2. Thermal stability of the urea complex with cetane in aqueous solutions: 1 —solubility of urea in water, 2 —thermal stability of the complex

Figure 2: Fig. 2. Thermal stability of the urea complex with cetane in aqueous solutions: 1 —solubility of urea in water, 2 —thermal stability of the complex

of the tube in the thermostat over several hours. If the complex is destroyed at the temperature at which the solubility and stability curves intersect, then when the temperature is lowered by 10–15° not only does the complex fail to form, but urea also does not precipitate from its supersaturated solution. In a control sealed tube without cetane (paraffin, ceresin), however, crystallization of urea began when the solution was supercooled by 1–1.5°.

Fig. 2. Thermal stability of the urea complex with cetane in aqueous solutions: **1** —solubility of urea in water, **2** —thermal stability of the complex.

The reason for the delay in crystallization of the complex may be seen in the low probability of formation of a complex nucleus, if one takes into account that, for example, in the urea complex with cetane there are twelve urea molecules per one cetane molecule (7). The delay in crystallization of urea in the presence of cetane (paraffin, ceresin) may be explained by adsorption of cetane (paraffin, ceresin) molecules on the surface of the urea nucleus, which prevents further growth of the nucleus.

Thus, using urea complexes with ceresin as an example, it has been shown that the melting point of urea (132.7°) is not the limit above which the complex cannot exist. The urea complex with synthetic ceresin is stable up to 141.0°.

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Note: Figure translations are in progress. See original paper for figures.