[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE BROOKLYN COLLEGE OF PHARMACY]

Ternary Systems of Urea and Acids. IV. Urea, Citric Acid and Water. V. Urea, Acetic Acid and Water. VI. Urea, Tartaric Acid and Water

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In a previous publication[1] dealing with a phase rule study of the solubility relations of aqueous solutions of urea and acids, solubility measurements were reported for the three ternary systems of urea with nitric, sulfuric and oxalic acids. The existence of one or more double compounds was established in each system.

The present investigation is a continuation of this study and presents the results obtained in the determination of the three ternary systems consisting of urea, water and each of the following: citric, acetic and tartaric acids.

Materials

Urea.—The urea used was Mallinckrodt "Analytical Reagent." After recrystallization, analyses by the standard urease method[2] showed an average urea content of 99.8%.

Acetic Acid.—Merck C. P. acid was purified by freezing and preserved in a well-stoppered container. Titration with standard alkali indicated that it was 99.8% pure.

Citric and Tartaric Acids.—The anhydrous citric and d-tartaric acids were presented by Charles Pfizer and Company. Both of these acids were dried and stored over sulfuric acid. Titration against sodium hydroxide showed that the citric and tartaric acids averaged 99.9% and 99.8% of their theoretical values, respectively.

Standard Sodium Hydroxide.—This solution was prepared and used according to accepted standards. It was protected against dust, etc., and restandardized at regular intervals.

Procedure.—The description of the apparatus and the method of analysis of the saturated solutions has already been presented in a previous publication.[1] After the original complexes had been rotated to equilibrium at constant

temperature, samples were withdrawn for the determination of acid by titration with alkali using phenolphthalein as indicator. Measurements for urea were made by the action of urease obtained from jack bean flour. The corresponding amount of ammonia liberated was taken up by hydrochloric acid and the excess acid titrated against alkali. Water was determined by difference.

This method for determining urea was used in the citric and tartaric acid systems with good results but proved unsatisfactory in the acetic acid system. The high values obtained for urea appear to be due to the fact that acetic acid is lost during the process of aeration for the removal of carbon dioxide. However, this easy volatility of acetic acid suggested an alternate method for the determination of urea which gave satisfactory results. A few cc. of the saturated solution was pipetted into a weighed porcelain crucible and evaporated to dryness in an oven maintained at 50-55°. The residue of urea was then dried to constant weight over sulfuric acid. By this method urea could be measured with an accuracy well within the limit of the urease method.

The composition of the original complexes and the solubility data obtained from the analyses of the saturated solutions have been expressed in weight per cent. and assembled in Tables I–III. The compositions of the solutions at the isothermally invariant points are the average of two or more closely agreeing results and not that of a single determination as the appearance of the isotherm would seem to indicate. In the last column are indicated the saturating solid phases which in the interest of economy of space have been abbreviated as follows: Ur for urea; C for $H_3C_6H_5O_7$; Ur·C for $CO(NH_2)_2·H_3C_6H_5O_7$; Ur_2·C for $[CO(NH_2)_2]_2·H_3C_6H_5O_7$; Ur_4·C for $[CO(NH_2)_2]_4·H_3C_6H_5O_7$; HAc for $HC_2H_3O_2$; Ur·AC_2 for $CO(NH_2)_2·2HC_2H_3O_2$; T for $H_2C_4H_4O_6$; Ur_2·T for $[CO(NH_2)_2]_2·H_2C_4H_4O_6$; and Ur·$T_2$ for $CO(NH_2)_2·2H_2C_4H_4O_6$.

The identification of the various saturating solid phases was established by the method of extrapolation of the tie lines and confirmed by the analysis of the solids found in

(1) Dalman, THIS JOURNAL, **56**, 549 (1934).

(2) Fox and Geldard, Ind. Eng. Chem., **15**, 743 (1923).

TABLE I
UREA-CITRIC ACID-WATER

Original complex Wt., % Urea	Wt., % H₃C₆H₅O₇	Saturated soln. Wt., % Urea	Wt., % H₃C₆H₅O₇	Solid phase
				10°
..	..	46.0	0.0	Ur
50.0	2.7	45.9	2.9	Ur
48.0	6.0	45.9	5.2	Ur + Ur₄·C
43.0	9.0	42.2	6.3	Ur₄·C
40.0	10.0	39.0	7.8	Ur₄·C
36.0	13.0	35.0	9.6	Ur₄·C + Ur₂·C
30.0	13.0	29.5	10.4	Ur₂·C
25.0	14.0	24.6	12.1	Ur₂·C
20.0	20.0	18.8	14.3	Ur₂·C + Ur·C
13.0	22.0	12.0	17.2	Ur·C
9.0	28.0	7.2	22.4	Ur·C
5.0	35.0	3.0	31.0	Ur·C
3.0	45.0	1.5	42.9	Ur·C
3.0	51.0	1.2	48.7	Ur·C
2.0	56.0	1.0	54.0	Ur·C + C
..	..	..	54.0	C
				25°
..	..	54.5	0.0	Ur
57.0	5.0	53.6	5.4	Ur
55.0	12.0	52.5	10.5	Ur + Ur₄·C
50.0	15.0	49.4	12.5	Ur₄·C
47.0	18.0	46.2	15.0	Ur₄·C
44.0	21.0	43.0	17.8	Ur₄·C + Ur₂·C
38.0	22.0	38.0	19.3	Ur₂·C
33.0	24.0	32.5	21.7	Ur₂·C
28.5	27.5	28.2	23.8	Ur₂·C + Ur·C
23.0	27.0	22.9	24.0	Ur·C
18.0	28.0	17.6	24.4	Ur·C
13.0	31.0	12.1	27.0	Ur·C
8.0	39.0	6.1	34.6	Ur·C
6.0	45.0	4.0	41.6	Ur·C
5.0	55.0	2.4	51.7	Ur·C
3.0	65.0	1.4	62.2	Ur·C + C
..	..	..	62.1	C
				40°
..	..	62.3	0.0	Ur
63.0	6.0	60.2	6.5	Ur
61.0	11.0	58.5	11.7	Ur
59.0	18.0	56.6	17.7	Ur + Ur₄·C
53.0	22.0	52.8	20.4	Ur₄·C
50.0	25.0	49.7	23.7	Ur₄·C
47.0	29.0	46.7	27.0	Ur₄·C + Ur₂·C
43.0	30.0	43.2	28.7	Ur₂·C
40.0	32.0	40.1	30.3	Ur₂·C
36.5	36.0	37.0	32.1	Ur₂·C + Ur·C
29.6	36.0	30.0	32.4	Ur·C
22.0	38.0	21.7	34.1	Ur·C
13.0	42.0	12.1	39.4	Ur·C
7.0	50.0	5.7	48.1	Ur·C
5.0	58.0	3.0	56.0	Ur·C
4.0	65.0	2.3	64.0	Ur·C
2.5	70.5	1.8	69.0	Ur·C + C
..	..	..	68.6	C

TABLE II
UREA-ACETIC ACID-WATER

Original complex Wt., % Urea	Wt., % HC₂H₃O₂	Saturated solution Wt., % Urea	Wt., % HC₂H₃O₂	Solid phase
				10°
..	..	46.0	0.0	Ur
48.0	7.0	45.9	7.3	Ur
47.0	14.0	45.5	14.4	Ur
47.0	21.0	44.8	21.8	Ur
46.0	28.0	43.6	29.3	Ur
45.0	35.0	42.3	36.7	Ur
43.0	42.0	41.7	40.7	Ur + Ur·Ac₂
36.0	47.0	36.4	44.0	Ur·Ac₂
27.0	55.0	25.8	52.9	Ur·Ac₂
19.0	65.0	17.2	64.7	Ur·Ac₂
14.0	75.0	12.3	75.6	Ur·Ac₂
10.0	85.0	8.5	86.0	Ur·Ac₂
10.0	88.0	7.0	90.5	Ur·Ac₂
7.0	92.0	6.5	91.8	Ur·Ac₂ + HAc
2.0	95.0	2.5	94.1	HAc
4.0	96.0	4.4	95.6	HAc
				25°
..	..	54.5	0.0	Ur
55.0	10.0	52.7	10.4	Ur
53.0	19.0	50.8	19.8	Ur
51.0	29.0	48.0	30.7	Ur
50.0	38.0	45.3	41.5	Ur
43.0	50.0	42.6	50.2	Ur + Ur·Ac₂
36.5	56.0	37.0	54.4	Ur·Ac₂
31.0	61.0	30.5	59.9	Ur·Ac₂
24.0	69.0	22.8	69.3	Ur·Ac₂
19.0	77.0	17.1	78.4	Ur·Ac₂
14.0	85.7	11.2	88.5	Ur·Ac₂
				40°
..	..	62.3	0.0	Ur
64.0	9.0	59.6	10.2	Ur
59.0	19.0	56.6	20.1	Ur
56.0	29.0	52.6	31.3	Ur
54.0	37.0	49.0	40.9	Ur
50.0	47.0	44.8	51.8	Ur
45.0	55.0	43.1	56.7	Ur
39.0	61.0	39.3	60.6	Ur·Ac₂
37.0	63.0	37.0	62.7	Ur·Ac₂
35.0	65.0	35.5	64.2	Ur·Ac₂
33.3	66.7	33.2	66.3	Ur·Ac₂
31.0	69.0	29.7	69.9	Ur·Ac₂
28.0	72.0	27.0	72.8	Ur·Ac₂

the sample tubes or of crystals grown by isothermal evaporation of solutions calculated to precipitate the desired solid phase. In either case the solid was separated from the saturated solution by means of a Gooch crucible and well centrifuged before analysis.

Results

The solubility of citric acid was measured by titration with approximately tenth normal sodium hydroxide using phenolphthalein as indicator. A survey of the literature for existing data with

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TABLE III

UREA–TARTARIC ACID–WATER

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Original complex Wt., % Urea	Wt., % $H_2C_4H_4O_6$	Saturated solution Wt., % Urea	Wt., % $H_2C_4H_4O_6$	Solid phase
			10°	
..	..	46.0	0.0	Ur
49.0	7.0	46.0	8.4	Ur
49.0	15.0	46.0	15.8	Ur
49.0	23.0	46.0	24.3	Ur
48.0	34.0	46.0	32.8	Ur + Ur₂·T
41.0	38.0	40.6	36.1	Ur₂·T
37.0	42.0	35.8	40.0	Ur₂·T
34.0	45.0	32.3	43.4	Ur₂·T
30.0	48.0	30.0	46.2	Ur₂·T + Ur·T₂
25.0	48.0	25.5	45.9	Ur·T₂
20.0	49.0	20.3	45.9	Ur·T₂
15.0	50.0	14.6	46.3	Ur·T₂
10.0	51.0	9.3	48.2	Ur·T₂
6.0	54.0	5.1	51.7	Ur·T₂
5.0	55.0	4.6	54.3	Ur·T₂
5.0	58.0	4.7	55.9	Ur·T₂ + T
3.0	57.0	3.1	55.5	T
..	..	..	54.5	T
			25°	
..	..	54.5	0.0	Ur
57.0	8.0	53.2	8.7	Ur
56.0	16.0	51.8	17.5	Ur
55.0	25.0	50.3	27.7	Ur
51.0	36.0	49.0	35.9	Ur + Ur₂·T
44.0	41.0	43.9	39.6	Ur₂·T
39.0	46.0	38.0	44.4	Ur₂·T
33.5	50.5	33.5	48.8	Ur₂·T + Ur·T₂
25.0	52.0	25.6	49.7	Ur·T₂
20.0	53.0	20.3	50.5	Ur·T₂
15.0	55.0	14.7	51.6	Ur·T₂
9.0	57.0	8.4	54.6	Ur·T₂
7.0	60.0	6.0	56.6	Ur·T₂
5.5	61.0	5.0	59.1	Ur·T₂ + T
3.0	61.0	3.2	58.8	T
..	..	..	58.5	T

which to compare the data obtained showed but a single reference, namely, that of Seidell[3] whose value given only at 25° was reported to be 61.71%. This compares favorably with 62.08% found in this investigation (average of four determinations).

The solubility of tartaric acid measured by the same method at 25° was found to be 58.51% (average of five determinations). Seidell's figure for the corresponding solubility is given as 57.9%, while Leidie[4] reported 59.79%. At 10° the solubility of Leidie is likewise about 1% higher than the value reported here in Table III.

Since these solubilities were measured by the same method the lack of agreement appears to

(3) Seidell, Bull. No. 67, Hyg. Lab., 1910.
(4) Leidie, Compt. rend., 96, 87 (1887).

be due to the quality of the acids used in the investigation. In view of this fact, a systematic determination of the solubility of carefully purified citric and tartaric acids has been undertaken in this Laboratory.

IV. Urea, Citric Acid and Water

This system was studied at 10, 25 and 40°; solubility data are shown in Table I and graphed in Fig. 1. The isotherm at 40°, which is given in complete detail, consists of five solubility curves indicating the existence of five solid phases including three double salts. Reading from left to right, these solid phases are: urea for solutions between points a and b; tetraurea citrate for b–c; diurea citrate for c–d; monourea citrate for d–e; and anhydrous citric acid for e–f.

<div style="text-align:center">H₂O</div>

<div style="text-align:center">Urea   Ur₄·C Ur₂·C Ur·C   H₃C₆H₅O₇</div>
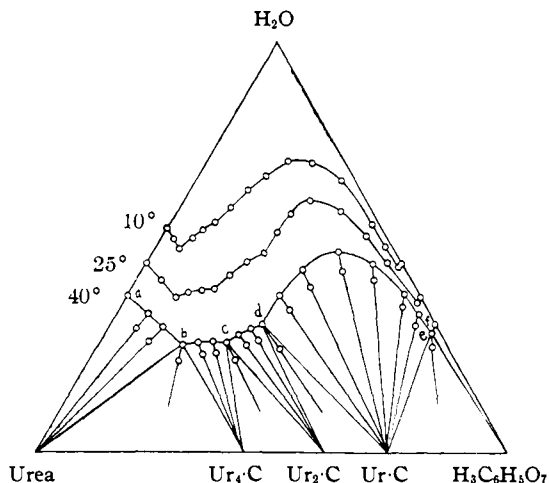
Fig. 1.—10, 25 and 40° isotherms.

The isotherms at 10 and 25° also contain five solubility curves and differ from that at 40° only in that the solid phase corresponding to the curve e–f is citric acid monohydrate instead of the anhydrous acid. This curve, of course, disappears from the system at the temperature of the transition of the monohydrate to the anhydrous acid which has been found to be 35.80°.

The Quintuple Point.—It is evident from these considerations that the curve for anhydrous citric acid originates between 25 and 40° and at the isothermally invariant point e when the system already contains vapor, solution and two solid phases. The introduction of fifth phase results in an invariant system possessing no degrees of freedom. By means of cooling curves this invariant temperature was found to be 33.73°. The composition of the saturated solution at the quin-

tuple point was not determined. Although the tie lines have been omitted from the 10 and 25° isotherms, their extrapolation to the proper solid phases has been found to be quite satisfactory.

Further, while not indicated, the curves a–b and d–e have been found to extend metastably into the area of the tetraurea citrate where they intersect to form a metastable isothermal invariant point.
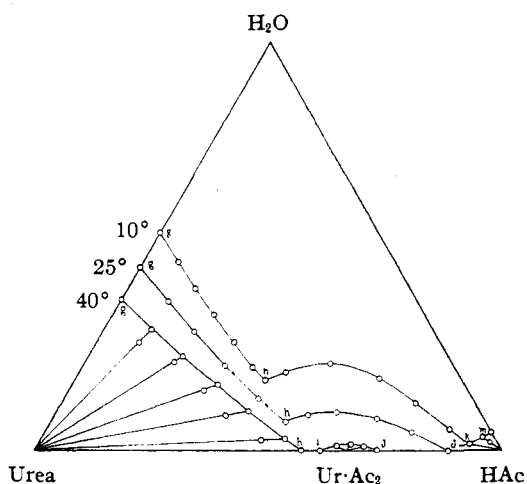

Fig. 2.—10, 25 and 40° isotherms.

It is possible to prepare the salts of monourea and diurea citrate in excellent purity since they form hard, well-defined crystals of considerable size which yield good analytical results.

	Calculated, %			Found, %		
	Urea	Acid	H₂O	Urea	Acid	H₂O
	Urea	Acid	H_2O	Urea	Acid	H_2O
Ur·C	23.82	76.18	0.00	23.7	75.7	0.60
Ur₂·C	38.47	61.53	.00	38.1	61.0	.90

Both of these salts have been prepared and described by previous investigators; monourea citrate by Hlasiwetz[5] and diurea citrate by Loschmidt.[6]

The tetraurea citrate, on the contrary, separates slowly from well-cooled solutions, or by proper seeding forming small, lustrous flakes which fail to develop into sizable crystals even on prolonged agitation in the thermostat. After being filtered rapidly and centrifuged at 300 r. p. m., the salt still showed 6–7% of water. Since the salt shows incongruent solubility, its composition could not be determined by evaporating its solutions to dryness. However, the tie lines extrapolated to the composition of tetraurea citrate with suitable accuracy. Moreover, the analyses of the centrifuged wet residue fell satisfactorily

(5) Hlasiwetz, J. prakt. Chem., **69**, 104 (1856).
(6) Loschmidt, Jahresb. Chem., 658 (1865).

on these tie lines and the salt is therefore reported as tetraurea citrate.

V. Urea, Acetic Acid and Water

This system was likewise investigated at 10, 25 and 40°; the experimental results are shown in Table II. The system has been found to produce only one double salt and this has been described by Du Toit.[7] The solubility curves are drawn in Fig. 2. Due to the high solubility of urea diacetate, the isotherms resemble those found in the sulfuric acid system.[1]

At 10° the isotherm consists of three intersecting curves which represent solutions in equilibrium with urea g–h, urea diacetate h–k, and solid acetic acid k–m. The latter curve is missing at 25°, and the curve for urea diacetate therefore terminates at the base line at the solubility of the double salt in pure acetic acid, j. The isotherm at 40° differs from those at 10 and 25° in that the curves for urea and diacetate no longer intersect but exist as two separate curves. This follows as a natural consequence of the downward movement of the isotherm with rising temperatures. Point h now represents the solubility of urea in acetic acid, while i and j denote the limits of solubility of urea diacetate in acetic acid. The curve for this salt has been enlarged somewhat in order to render a clearer picture of its scope.

While no tie lines have been drawn for the double salt, their extrapolation leaves little doubt as to its identity. On analysis it was found to contain: calcd. for $CO(NH_2)_2 \cdot 2HC_2H_3O_2$; urea, 33.34; acid, 66.66. Found: urea, 32.9; acid, 65.6; water, 1.5%.

The melting point of urea diacetate has been reported to be about 35° by Du Toit.[7] Since this solid phase was found to be stable at 40° it was decided to repeat this melting point determination. The results showed that the double salt melts slowly at 35° and more rapidly as the temperature is increased to 41° when the change is quite sudden. Inasmuch as this salt decomposes rapidly on exposure to air through the evaporation of acetic acid, the same decomposition undoubtedly occurs in the open capillary tube, and thus interferes with the melting point determination. This difficulty was eliminated satisfactorily in a closed tube in the following manner. A regular glass-stoppered solubility

(7) Du Toit, Verslag. Wetenschschappen, **22**, 573 (1913).

tube was loaded with urea and acetic acid in the proportions in which they occur in the salt. The contents were warmed until complete solution occurred and then cooled until only a small amount of crystals had formed. The tube was rotated in the bath and the temperature adjusted so that the quantity of crystals appeared to remain constant over a period of a few hours. This temperature was found to lie between 41.25 and 41.30°. However, in view of small impurities present in the urea and acid, the melting point of urea diacetate is reported to be 41.3°.

Above this temperature then the isotherm (providing no new phases enter the system) contains only the curve g–h which represents the solubility of urea ranging from pure water to pure acetic acid.

VI. Urea, Tartaric Acid and Water

In this system solubility measurements were made at 10 and 25°; these data are assembled in Table III. The isotherms which are drawn in Fig. 3 are very similar and consist of four curves which represent solutions in equilibrium with urea n–o, diurea tartrate o–p, urea ditartrate p–r and tartaric acid r–s. The solutions saturated with these double salts were found to be highly viscous.

Diurea tartrate, which has been prepared and described by Loschmidt,[6] was found to consist of rather soft crystals which gave the following results on analysis: calcd. for $U_2 \cdot T$: urea, 44.46; acid, 55.54. Found: urea, 43.4; acid, 54.5; water, 2.1%.

Urea ditartrate, which has been reported by Hlasiwetz,[5] crystallizes exceedingly slowly. As in the case of tetraurea citrate, this salt still

contained about 11% of water after being centrifuged thoroughly. However, the analyses of wet residues fell satisfactorily on the tie lines extrapolating to the composition of a 1:2 double salt and its identification is therefore considered to be suitably established.
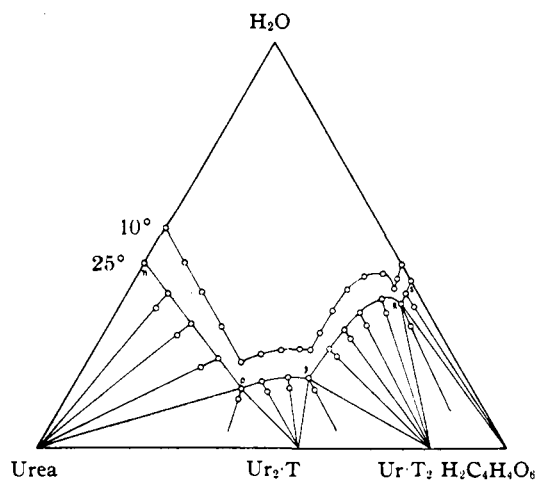

Fig. 3.—10 and 25° isotherms.

Summary

The solubility relationships in the systems urea–citric acid–water and urea–acetic acid–water have been studied at 10, 25 and 40°; the system urea–tartaric acid–water has been studied at 10 and 25°.

The following double salts were found to exist: tetraurea citrate, diurea citrate, monourea citrate, diurea tartrate, urea ditartrate and urea diacetate.

The urea diacetate has been found to exist only below 41.3°; citric acid monohydrate only below 35.80° and anhydrous citric acid only above 33.73°.