

LITERATURE CITED

- (1) Archer, G., Hildebrand, J. H., *J. Phys. Chem.*, **67**, 1830 (1963).
- (2) Cook, H. W., Hansen, D. N., Alder, B. J., *J. Chem. Phys.*, **26**, 748 (1957).
- (3) Dymond, J. H., *J. Phys. Chem.*, **71**, 1829 (1967).
- (4) Dymond, J. H., Hildebrand, J. H., *Ind. Eng. Chem. Fundam.*, **6**, 130 (1967).
- (5) Gjaldbaek, J. C., Hildebrand, J. H., *J. Amer. Chem. Soc.*, **71**, 3147 (1949).
- (6) Hiraoka, H., Hildebrand, J. H., *J. Phys. Chem.*, **68**, 213 (1964).
- (7) Horiuti, J., *Sci. Papers, Inst. Phys. Chem. Res., Tokyo*, **17**, No. 341, 125 (1931).
- (8) Kobatake, Y., Hildebrand, J. H., *J. Phys. Chem.*, **65**, 331 (1970).
- (9) Linford, R. J., Hildebrand, J. H., *Trans. Faraday Soc.*, **66**, 577 (1970).
- (10) Miller, K. W., *J. Phys. Chem.*, **72**, 2248 (1968).
- (11) Powell, R. J., Hildebrand, J. H., *J. Chem. Phys.*, **55**, 4715 (1971).
- (12) Reeves, L. W., Hildebrand, J. H., *J. Amer. Chem. Soc.*, **79**, 1313 (1957).

RECEIVED for review August 13, 1971. Accepted January 20, 1972. Work supported by the National Science Foundation.

Solubility of Urea in Water-Alcohol Mixtures

FU-MING LEE and LESLIE E. LAHTI¹

Department of Chemical Engineering, The University of Toledo, Toledo, OH 43606

The solubility of urea in water, methyl alcohol, ethyl alcohol, isopropyl alcohol, and mixtures thereof was experimentally measured over a temperature range from about 0–60°C. The data were correlated by an exponential function of the form:

$$\log S = A + B/T$$

The actual data and constants for the correlating equation are reported.

Many of the processes concerned with nucleation and crystallization of urea are not well understood. In addition, the solubilities of urea in water-alcohol mixtures, which have to be known to study the nucleation process, have not been measured to any great extent. The data available in the literature are quite scattered and in some cases believed to be unreliable.

The object of this investigation (2) was to determine systematically the solubility of urea in water, methanol, ethanol, isopropanol, and their mixtures. The results were compared with some literature values existing for the pure solvents.

EXPERIMENTAL

Saturated solutions of urea in 12 different solvents were prepared at temperatures from about 0–60°C. The particular solvent and an excess amount of urea were added to a 300-ml round-bottomed flask. The flask with urea and solvent was then placed in the constant-temperature bath at a predetermined temperature, controlled to within $\pm 0.05^\circ\text{C}$. For bath temperatures below room temperature, cooling was provided from a coolant reservoir. A constant flow cooler made by Blue M (Model No. PLL-24SSA-2) was used to maintain the temperature in the coolant reservoir. The solution in the flask was agitated by a glass rod stirrer for at least 6 hr to reach saturation as previously determined (8). Dirnhuber and Schutz (1) have established that conversion to ammonium cyanate amounts to about 0.1% when held for periods of less than 2 days. After saturation, the solution was allowed to settle for about 1 hr. The top part of the clear solution was transferred by means of a 50-ml syringe and an 18-gauge needle to a tared

sealed bottle stored in an oven at a temperature a few degrees higher than the saturation temperature.

About 3–5 ml of saturated solution was transferred into the weighing bottle, immediately covered, and weighed again. All the weighings were made on an Ainsworth (Type 10) single-pen analytical balance reading to 10^{-4} grams. The sample was dried in an oven at 40°C for 12 hr and then placed in a vacuum desiccator for at least 4 hr until a constant weight was achieved. The vacuum step was used to speed up the drying process and to minimize the decomposition of urea at the higher temperatures needed for drying at atmospheric pressure. Finally, the bottle with dried crystals was weighed again, from which the solubility data were calculated. To determine the experimental error, replications of experiments were made for each temperature with three samples taken for each case, and the average values were considered to be the results. The reproducibility of the data was within $\pm 0.5\%$. Recrystallization of urea in water showed no change in the solubility.

MATERIALS

Certified ACS-grade urea (minimum purity of 99.976%) from Matheson, Coleman & Bell was used as the solute. Methanol and isopropanol were also certified ACS grade from Fisher. Absolute ethanol was purchased from Commercial Solvents, and the water was doubly distilled.

DISCUSSION

The experimental solubilities are presented in Tables I–III. A General Electric Time Sharing Computer Mark 1 was used to

¹ To whom correspondence should be addressed.

Table I. Solubility of Urea in Pure Solvents

Water		Methanol	
<i>t</i> , °C	<i>S</i> , g/100 g	<i>t</i> , °C	<i>S</i> , g/100 g
1.8	70.12	0.15	7.646
10.3	85.86	7.1	10.68
15.5	97.00	10.6	12.65
21.0	109.6	15.9	19.78
25.5	121.0	20.0	21.79
30.5	135.4	24.7	24.11
39.7	163.9	30.9	28.28
50.1	205.2	40.3	36.42
60.0	258.9	43.0	39.00

Ethanol		Isopropanol	
<i>t</i> , °C	<i>S</i> , g/100 g	<i>t</i> , °C	<i>S</i> , g/100 g
6.9	3.717	0.1	1.679
18.2	4.877	16.3	2.573
25.5	5.837	20.7	2.840
35.5	7.444	25.3	3.172
45.4	9.681	37.7	4.288
55.0	12.44	44.8	5.021
65.4	16.94	50.4	5.789
		60.2	7.194

Table II. Solubility of Urea in Alcohol Mixtures^a

50% Methanol-50% ethanol		50% Ethanol-50% isopropanol	
<i>t</i> , °C	<i>S</i> , g/100 g	<i>t</i> , °C	<i>S</i> , g/100 g
5.5	7.726	7.0	2.495
7.0	8.174	16.5	3.156
15.5	9.826	25.3	4.004
25.1	12.26	36.2	5.275
35.3	15.88	45.4	6.680
44.8	20.55	55.4	8.642
55.2	27.93	69.4	12.82
64.6	39.24		

50% Methanol-50% isopropanol	
<i>t</i> , °C	<i>S</i> , g/100 g
1.8	4.954
12.1	6.114
16.4	6.819
21.4	7.657
25.5	8.425
31.3	9.711
39.8	12.36
49.8	15.99

^a The solvent mixtures are by volume percent.

find the correlation between urea solubility and temperature, using the method of least squares. Six different mathematical models were considered with the best correlation of the form,

$$\log_e S = A + Bt$$

The values of *A* and *B* are given in Table IV along with the standard percent deviation. The same relationships were indicated by previous investigators (3, 5, 7, 9) for the solubilities of urea in water and ethanol. The solubility of urea in alcohol mixtures was shown to be predictable, from the values in pure solvents, by using a linear combination of the mole fractions of the solvents. For water-alcohol mixtures, the linear combination method did not work, probably because of the difference in solvent molecular structures.

The solubility of urea in methanol exhibited a different behavior from the other solvents in that a separate correlation was found in the low-temperature range of 0 to 15°C apart from that of 15–43°C. In the lower temperature range, the solubility increased exponentially faster with temperature than at the higher temperatures. Similar deviations were found with

Table III. Solubility of Urea in Water-Alcohol Mixtures^a

33.3% Water-66.7% isopropanol		33.3% Water-66.7% ethanol	
<i>t</i> , °C	<i>S</i> , g/100 g	<i>t</i> , °C	<i>S</i> , g/100 g
7.0	30.01	5.4	34.55
16.0	37.74	15.8	44.19
25.1	47.56	24.9	55.06
36.2	62.18	35.2	70.83
43.9	75.72	45.7	92.15
53.8	98.75	55.0	118.0
62.8	125.0	63.8	149.6

66.7% Water-33.3% isopropanol		66.7% Water-33.3% ethanol	
<i>t</i> , °C	<i>S</i> , g/100 g	<i>t</i> , °C	<i>S</i> , g/100 g
6.3	58.67	6.2	59.17
16.5	76.68	15.1	74.68
25.7	94.55	24.9	94.83
35.7	118.7	35.1	119.9
45.7	149.3	44.6	147.5
55.0	184.1	54.6	187.9
63.8	226.2	63.9	230.2

50% Water-50% methanol	
<i>t</i> , °C	<i>S</i> , g/100 g
0.3	46.42
10.5	60.33
20.6	77.91
24.6	85.72
35.0	109.5
44.5	139.0
55.1	176.0

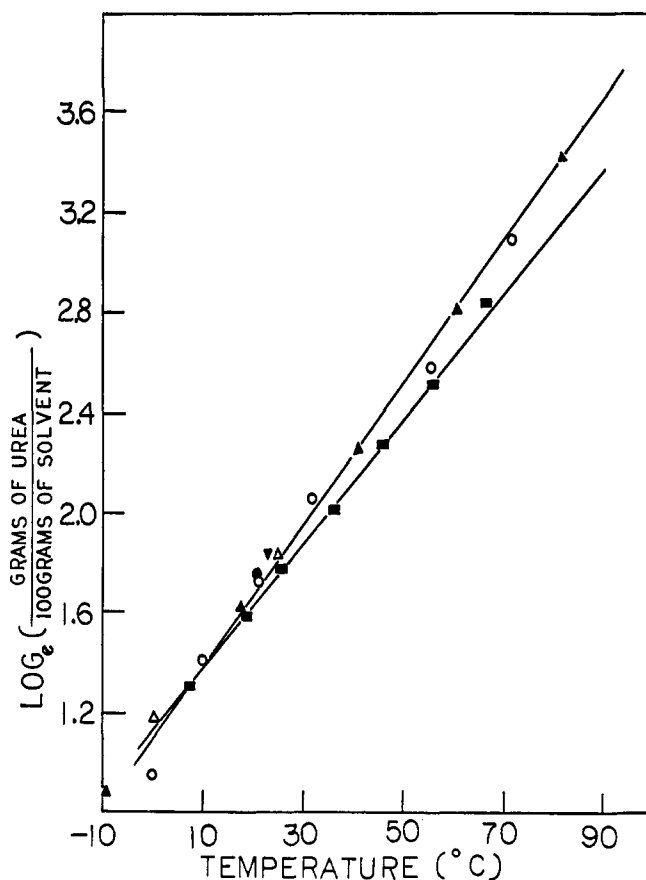
^a The solvent mixtures are by volume percent.

Figure 1. Comparison of Solubility of Urea in Ethanol

- Tamarelli and Manning (1967)
- Speyers (1902)
- △ Osaka and Ando (1921)
- ▼ Pucher and Dehn (1921)
- ▲ Timofeiev (1894)
- This work (1971)

Table IV. Constants of Correlating Equation
 $\log S = A + Bt$

Solvents	A	B	Std % dev
Water	4.225	0.0216	0.14
Methanol	2.573	0.0252	0.25 ^a
Ethanol	1.129	0.0251	0.46
Isopropanol	0.538	0.0241	1.60
50% Methanol- 50% ethanol	1.912	0.0244	0.50
50% Ethanol- 50% isopropanol	0.723	0.0261	0.51
50% Methanol- 50% isopropanol	1.522	0.0247	0.94
33.3% Water- 66.7% isopropanol	3.217	0.0256	0.16
33.3% Water- 66.7% ethanol	3.392	0.0251	0.24
66.7% Water- 33.3% isopropanol	3.944	0.0232	0.18
66.7% Water- 33.3% ethanol	3.954	0.0234	0.22
50% Water- 50% methanol	3.844	0.0243	0.16

^a Over temperature range 15.9–43.0°C.

the other solvents, but at lower temperatures (about 0–5°C). A consistent deviation between the best fit values and the experimental values was observed at the elevated temperatures. The maximum deviations occurred with methanol as the solvent, namely about 5% higher for pure methanol at 55°C, and about 18.5% higher at 64.5°C for the mixture of 50% methanol–50% ethanol. The deviations exhibited with other solvents at the higher temperatures were not so severe as with methanol mixtures. This phenomenon might be due to the higher volatility of methanol and hence not so easy to correlate with a simple exponential function.

The solubilities of urea in ethanol and water measured in this investigation were compared with literature values. Figure 1 shows that the solubilities in ethanol were lower than those reported by Timofeiew (10) above 25°C, but compared favorably at lower temperatures with some of Speyers' (7) values. However, the data of 70 years ago may also reflect differences in water content of the absolute ethanol. The solubility of urea in water is about 20 times higher than that in ethanol, and even trace amounts of water cause tremendous increases in solubility. The solubility data obtained in this work were correlated by the exponential function with a standard deviation of only 0.46%, while the literature values exhibited some serious scattering. For water as the solvent (Figure 2), the solubility values from this work were consistent with those of Pinck and Kelly (5) except at about 60°C. Speyers' (7) data differed at all temperatures above 10°C. From these comparisons, it was felt that the experimental methods used in this investigation were reliable for determining the solubilities of urea in water–alcohol mixtures. For methanol or methanol mixtures, this method should not be used for temperatures above 55°C.

NOMENCLATURE

A, B = empirical constants varying with the solvent
 S = solubility in grams of urea per 100 grams of solvent
 t = temperature in °C

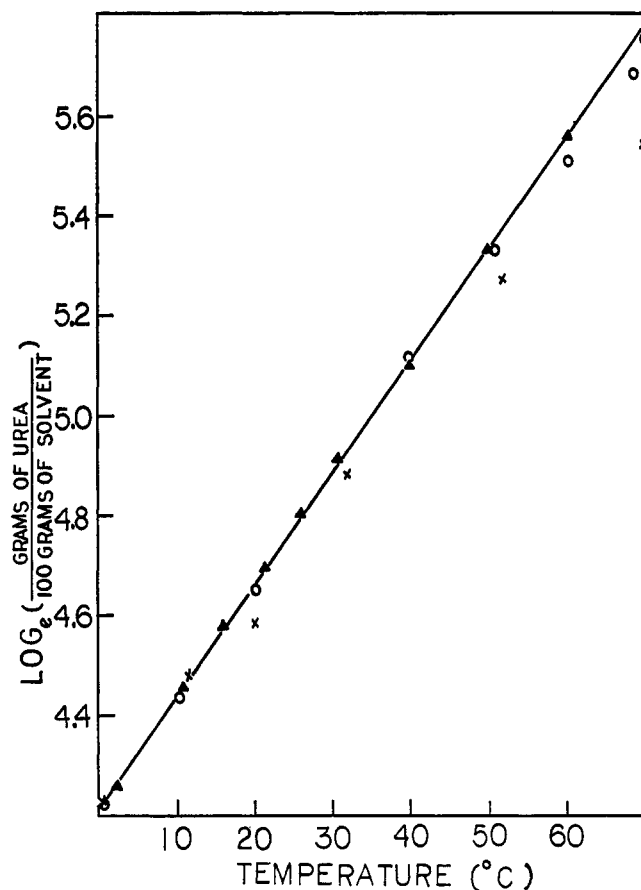


Figure 2. Comparison of Solubility of Urea in Water

× Speyers (1902)
 ○ Pinck and Kelly (1925)
 ▲ This work (1971)

LITERATURE CITED

- (1) Dirnhuber, P., Schutz, F., *Biochem. J.*, **42**, 628 (1948).
- (2) Lee, F. M., MS ChE Dissertation, University of Toledo, Toledo, OH (1971).
- (3) Miller, F. W., Dittmar, H. R., *J. Amer. Chem. Soc.*, **56**, 848 (1934).
- (4) Osaka, Y., Ando, K., Kyoto University (1921) as reported in Seidell, "Solubilities of Organic Compounds," 3rd ed., D. Van Nostrand Co., New York, NY (1941).
- (5) Pinck, L. A., Kelly, M. A., *J. Amer. Chem. Soc.*, **47**, 2170 (1925).
- (6) Pucher, G., Dehn, W. M., *ibid.*, **43**, 753 (1921).
- (7) Speyers, C. L., *Amer. J. Sci. (IV)*, **14**, 293 (1902).
- (8) Storm, T. D., Hazleton, R. A., Lahti, L. E., *J. Cryst. Growth*, **7**, 55 (1970).
- (9) Tamarelli, A. W., Manning, F. S., *AIChE J.*, **13** (2), 241 (1967).
- (10) Timofeiew, W., Dissertation (Kharkov-1894) as Reported in Seidell, "Solubilities of Organic Compounds," 3rd ed., Van Nostrand Co., New York, NY (1941).

RECEIVED for review August 16, 1971. Accepted February 21, 1972. Work supported by the National Science Foundation and the University of Toledo.