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## Solubility of Urea in ethanol-water mixtures and pure ethanol from 278.1K to 333.1K

## Solubilidad de Urea en mezclas de etanol-agua y etanol puro a temperaturas de 278,1K a 333,1K

# Solubilidade da Ureia em misturas de etanol-água e em etanol puro em temperaturas de 278,1K a 333,1K

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## Abstract

This paper deals with the solubility of urea in ethanol-water mixtures in mole fractions of ethanol between 0.0901 and 1.000 at temperatures ranging from 278.1 to 333.1K. The investigation of solubility contributes to research in many others fields of study in chemical engineering, since there are several studies where the solubility of urea and its behavior in solution influence the system. The experiment was carried out at constant temperature, stirring for 2h and then leaving the solution at rest for 2h. After collecting the data, the solubility of urea was calculated based on the gravimetric method. The experimental results obtained were correlated with the temperature of the solvents using three equations based on the literature. The three models demonstrated results in line with the experimental data. It was observed that adding ethanol to the water decreased urea solubility in all cases. The differences between the predicted and the experimental values were on average 4.7%.

Keywords: urea, ethanol, gravimetric method, solubility.

## Resumen

Este artículo trata de la solubilidad de la urea en mezclas de etanol-agua en fracciones molares de etanol entre 0,0901 y 1,000 a temperaturas de 278,2 a 333,2K. La investigación de la solubilidad contribuye en muchos estudios en muchos otros campos de estudio en ingeniería química, ya que hay varios estudios en que la solubilidad de la urea y su comportamiento en solución influyen en el sistema. El experimento se llevó a cabo a temperatura constante, se agitó durante 2h y en seguida la solución se dejó en reposo también por 2h. Después de recoger los datos, la solubilidad de la urea se calculó basándose en el método gravimétrico. Los resultados experimentales obtenidos se correlacionaron con la temperatura de los disolventes usando tres ecuaciones basadas en la literatura. Los modelos han demostrado resultados en línea con los datos experimentales. Se observó que la adición de etanol al agua disminuye la solubilidad de la urea en todos los casos. Las diferencias entre los predichos y los valores experimentales fueron en promedio de 4,7%.

Palabras clave: etanol, método gravimétrico, solubilidad.

## Resumo

Este artigo trata da solubilidade de uréia em misturas de etanol-água em frações molares de etanol entre 0,0901 e 1,000 e temperaturas que variam de 278,1 a 333,1K. A investigação de solubilidade contribui para a pesquisa em muitos outros campos de estudo em engenharia química, uma vez que há vários estudos em que a solubilidade da ureia e o seu comportamento em solução influenciam o sistema. O experimento foi realizado a uma temperatura constante com agitação de 2h e, em seguida, deixando a solução em repouso durante 2h. Depois de recolher os dados, a solubilidade da ureia foi calculada com base no método gravimétrico. Os resultados experimentais obtidos foram correlacionados com a temperatura dos solventes utilizando três equações com base na literatura. Os três modelos demonstraram resultados condizentes com os dados experimentais. Observou-se que a adição de etanol na mistura provoca diminuição na solubilidade ureia em todos os casos. As diferenças entre os valores previsto e os experimentais foram, em média, 4,7%.

Palabras-chave: uréia, etanol, método gravimétrico, solubilidade.

## Introduction

Urea  $(NH_2-CO-NH_2)$  is the most commonly used nitrogen fertilizer in the world, due to their low value and high nitrogen content [1,2]. Urea has also many uses in chemical industries such as the manufacture of resins, medicines, cosmetics and cleaning products [1-6]. Besides, it has great biological importance, since it is the final metabolite of nitrogenous compounds in mammals [1,3,5].

The study of the solubility is important in the process of nucleation and crystallization [7-12]. The solubility of urea is not fully explored and the process has not been studied over wide ranges of temperature and solvents [13-14].

Since ancient times, some natural and industrial processes require information of mixtures in equilibrium phases containing, or not, electrolytes. Some examples are: precipitation and crystallization processes; water desalination; control of water pollution; extraction and distillation; food processing, production of fertilizer among others [15].

Data regarding chemical compounds solubility in water and solvent mixtures are fundamental in designing of industrial separation equipment such as crystallizers, extractors, evaporators and absorption units.

The solubility of organic compounds in water is an important data in chemical, pharmaceutical, food industries, and environmental applications [16]. The lack of experimental solubility data of solutes in solvents limits the development of predictive models [17].

The study of the water-organic phase behavior is essential in the design of separation process and operation of separation units in the chemical industry and in related industries [11]. In many cases a complete equilibrium data is practically impossible due to the long time taken to get them and also by the high cost of analysis. Thus, models and parameters are obtained by a minimum number of experiments [18]. Data on the solubility of urea in aqueous ethanol solution are essential for industrial design and further theoretical studies [10,11]. In this paper, the solubility of urea in pure ethanol and in ethanol and water mixtures (0.0901; 0.2096 and 0.3757 of ethanol) at temperatures ranging from 278.2 to 333.2K was systematically measured by gravimetric method. The results were correlated using different equations available in the literature.

## **Experimental**

## Materials

Urea with 99.5% (in mass) purity and ethanol with a purity of 99.8% (in mass) were purchased from Nuclear and Vetec, respectively. Deionized (E. J. Krieger & Cia. Ltd., model Permution) and distilled (Quimis, model G.341.25) water was used in the experiments. All chemicals were used without further purification.

#### **Experimental apparatus**

The solubility of urea was measured using an equilibrium cell similar to that reported in the literature [10-14]. The solubility of urea was determined in a temperature range from 278.2 to 333.2K at atmospheric pressure (92654.3Pa), in pure ethanol and mixtures of water and ethanol with ethanol mole fractions of 0.0901, 0.2096 and 0.3757, in a previously prepared solution using analytical balance (Gehaka, AY-220± 0.0001g).

A jacketed borosilicate glass cell with capacity of 40.0mL and with sampling points at the side was

used in this work. Urea was added in excess to the solution, which was stirred for two hours using a magnetic stirrer (Marconi, MA-089).

Subsequently, the system was left decanting for two hours, keeping the temperature control of the cell through a thermostatic bath (Marconi, MA-184). A thermocouple (Full-Gauge, TIC-17RGTi  $\pm$  0.1K), which was calibrated using an Incoterm standard thermometer ( $\pm$  0.1K), was used to measure the temperature inside the cell. The experimental apparatus can be seen in Figure 1.



Figure 1. The experimental apparatus: (A) Equilibrium cell; (B) Magnetic stirrer; (C) Latex hose; (D) Thermocouple; (E) Thermostatic bath.

For each temperature, four samples were drawn using a glass syringe (10mL, Artiglass) to check the reproducibility of the procedure. The samples were quantified by gravimetric analysis, remaining 48h in a stove (Medicate, MD-1.3) at 338.2K. After the drying period, the samples containing crystallized urea was placed in a desiccator with silica for 30min, then the molar fraction of dry urea was quantified to determinate the value of solubility. Four solubility values  $(x_{exp})$  were determined for each temperature. Afterwards, the average of those four measurements was computed. Equation 1 was used to calculate the mole fraction solubility [10]:

$$x_{\rm exp} = \frac{m_1/M_1}{m_1/M_1 + m_2/M_2 + m_3/M_3}$$
(1)

where  $m_{1^{\prime}}$   $m_{2}$  and  $m_{3}$  represent the mass of the solute (urea), solvent (water, ethanol) and ethanol only, respectively.  $M_{1}$ ,  $M_{2}$  and  $M_{3}$  are the respective molecular weights.

#### **Results and Discussion**

#### **Experimental data**

Table 1 contains solubility data experimentally obtained for the urea in a mixture of ethanol and water with ethanol mole fraction of 0.0901; 0.2096 and 0.3757 and in pure ethanol. This table also reports standard deviations ( $\delta$ ) of the value of solubility for each temperature and shows data available in the Lee and Lahti's [13] work for urea in ethanol and water mixtures in compositions of 0.1242 and 0.3095 (mole fraction) and in pure ethanol. These results were used for comparison and validation of the data found on this paper.

Table 1. Experimental	solubility of urea in	ethanol-water mixtures	s and in pure ethan	ol at different temperatures
	along with the	e solubility of urea in Le	ee and Lahti [13].	

				$x_{_{ethanol}}$			
T (K) ± σ	0.0901	0.1242 <sup>[13]</sup>	0.2096	0.3095 <sup>[13]</sup>	0.3757	1.0000	1.0000 <sup>[13]</sup>
278.2± 0.4			0.1503±0.0116				
278.6				0.1331			
279.4		0.1748					
279.7 ± 0.4						0.0277±0.0010	
280.0							0.0277
$280.3 \pm 0.6$	0.1779±0.0014						
280.7 ± 0.0					0.1128±0.0033		
283.2± 0.4			0.1809±0.0014				
283.9 ± 0.1						0.0325±0.0008	
285.3 ± 0.1	0.2007±0.0018						
$286.6 \pm 0.3$					0.1252±0.0016		
288.2± 0.4			0.1956±0.0013				
288.3		0.211					
288.7 ± 0.5						0.0353±0.0006	

T (K) ± σ         0.0901         0.1242 <sup>(13)</sup> 0.2096         0.305 <sup>(13)</sup> 0.3757         1.0000         1.0000 <sup>(13)</sup> 288 9 ± 0.5         0.1486±0.0018         0.1486±0.0018         0.0361           289.0         0.1641         0.0361         0.0361           283.2 ± 0.5         0.2161±0.0007         0.0406±0.0010         0.0361           283.2 ± 0.4         0.2127±0.0041         0.0406±0.0010         0.0406±0.0010           293.2 ± 0.5         0.2535         0.1966         0.1485±0.0086         0.0406±0.0011           298.2 ± 0.4         0.2267±0.0107         0.0518±0.0008         0.0428           298.6 ± 0.9         0.2561±0.0057         0.228±0.0094         0.0663±0.0011           302.2 ± 0.5         0.2561±0.0057         0.224±0.0080         0.0663±0.0011           302.2 ± 0.5         0.2561±0.0057         0.224±0.0080         0.0663±0.0015           303.2 ± 0.4         0.2561±0.0057         0.224±0.0080         0.0654±0.0015           303.2 ± 0.4         0.2071±0.0044         0.2394         0.0691           305.4 ± 0.5         0.2074±0.0194         0.238±0.0015         0.0544           312.3 ± 0.5         0.3260±0.0131         0.2974±0.0194         0.2578±0.0099         0.0769±0.0010 <t< th=""><th></th><th></th><th></th><th></th><th><math>x_{_{ethanol}}</math></th><th></th><th></th><th></th></t<>					$x_{_{ethanol}}$			
288 9 0.5       0.1486±0.0018         289.0       0.1641         289.4       0.2161±0.0007         291.4       0.2127±0.0041         293.2± 0.4       0.2127±0.0041         293.2± 0.5       0.2382±0.0059         294.5± 0.6       0.2425         298.2± 0.4       0.2535         298.2± 0.4       0.2535         298.2± 0.4       0.2535         298.2± 0.4       0.2267±0.0107         298.4± 0.4       0.2267±0.0107         298.4± 0.4       0.2267±0.0107         298.4± 0.4       0.2267±0.0107         298.4± 0.4       0.2261±0.0057         302.8± 0.3       0.3004         302.8± 0.3       0.3004         302.8± 0.3       0.3004         307.7± 0.5       0.22661±0.0057         308.3       0.3004         308.3       0.3004         308.3       0.3004         308.3       0.3004         312.2± 0.4       0.3004         312.2± 0.4       0.3004         312.2± 0.4       0.3463±0.0075         312.2± 0.4       0.3463±0.0075         317.3± 0.4       0.3463±0.0016         317.3± 0.4       0.3463±0.0016         31	T (K) ± σ	0.0901	0.1242 <sup>[13]</sup>	0.2096	0.3095 <sup>[13]</sup>	0.3757	1.0000	<b>1.0000</b> <sup>[13]</sup>
289.0       0.1641         289.4       0.2161±0.0007       0.0361         293.2       0.2161±0.0007       0.0406±0.0010         293.2       0.2302±0.0059       0.1485±0.0086       0.0406±0.0010         293.9       0.2600±0.0055       0.1485±0.0086       0.1485±0.0086         297.9       0.2600±0.0055       0.1485±0.0086       0.0518±0.0008         298.4       0.2535       0.1966       0.0518±0.0008         298.7       0.2561±0.0057       0.0663±0.0011       0.0663±0.0011         302.2       0.2710±0.0154       0.22661±0.0057       0.2244±0.0080         303.2       0.3054±0.0056       0.2711±0.0044       0.2394       0.0662±0.0015         307.8       0.3054±0.0056       0.2711±0.0044       0.2382±0.0036       0.054         303.2       0.3054±0.0056       0.2711±0.0044       0.2382±0.0036       0.0692±0.0015         308.7       0.3054±0.0057       0.2244±0.0080       0.0691±0.0015       0.054         312.4       0.3054±0.0056       0.2711±0.0044       0.2382±0.0036       0.0691±0.0015       0.054         312.4       0.3045       0.2974±0.0194       0.2578±0.0099       0.0691±0.0015       0.0691±0.0015         313.2±0.4       0.3463±0.0075       0.313	288.9 ± 0.5					0.1486±0.0018		_
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294.5 ± 0.6       0.2600±0.0056         297.9 ± 0.2       0.2600±0.0056         298.1       0.2535       0.1966         298.2 ± 0.4       0.2257 ± 0.1007       0.0518±0.008         298.9 ± 0.5       0.2267±0.0107       0.0518±0.008         298.9 ± 0.5       0.1825±0.0024       0.0663±0.0011         302.8 ± 0.3       0.2710±0.0154       0.2028±0.0094         303.0 ± 0.2       0.2710±0.0154       0.2561±0.0057         303.2 ± 0.4       0.2561±0.0057       0.2244±0.0080         307.7 ± 0.5       0.3054±0.0056       0.2271±0.0044         308.2 ± 0.4       0.2771±0.0044       0.2394         308.2 ± 0.4       0.2071±0.0044       0.0820±0.0015         308.2 ± 0.4       0.2771±0.0044       0.0808±0.0015         308.2 ± 0.4       0.2974±0.0194       0.2382±0.0036         312.4 ± 0.4       0.2974±0.0194       0.2382±0.0036         312.4 ± 0.4       0.3463±0.0075       0.0691±0.0010         317.1 ± 0.3       0.3645±0.0075       0.2974±0.0194         318.2 ± 0.4       0.313±00163       0.2978±0.0099         318.4       0.3915±0.0161       0.2905         318.4       0.3978±0.0161       0.0904±0.0009         323.2 ± 0.4       0.3978±0.0161<	293.9 ± 0.5	0.2392±0.0059						
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298.2± 0.4       0.2267±0.0107       0.0518±0.0008         298.7       0.0518±0.0008       0.0428         298.9± 0.5       0.1825±0.0024       0.0663±0.0011         302.9± 0.5       0.2028±0.0094       0.2028±0.0094         303.2± 0.4       0.2561±0.0057       0.224±0.0080         307.7± 0.5       0.2771±0.0044       0.0820±0.0015         307.8± 0.3       0.3054±0.0056       0.2771±0.0044         308.4       0.2771±0.0044       0.0820±0.0015         308.4       0.2014       0.2578±0.0086         302.2± 0.4       0.2071±0.0044       0.2384         308.4       0.2014       0.054         308.4       0.2071±0.0044       0.2384         308.4       0.2071±0.0044       0.2384         308.4       0.2071±0.0044       0.2384         312.2± 0.4       0.3004       0.2382±0.0036         312.2± 0.4       0.3463±0.0075       0.0578±0.0099         317.1± 0.5       0.3463±0.0075       0.2578±0.0099         318.2± 0.4       0.3456       0.2905         318.2± 0.4       0.3459       0.2905         318.2± 0.4       0.3456       0.2905         318.2± 0.4       0.3532±0.0161       0.2954±0.0430	298.1		0.2535		0.1966			
298.6 ± 0.9       0.0518±0.0008       0.0428         298.7       0.1825±0.0024       0.0663±0.0011         302.8 ± 0.5       0.2028±0.0094       0.0663±0.0011         302.9 ± 0.5       0.2028±0.0094       0.2028±0.0094         303.2 ± 0.4       0.2561±0.0057       0.2244±0.0080         307.7 ± 0.5       0.2271±0.0154       0.06820±0.0015         307.8 ± 0.3       0.305±0.0056       0.2771±0.0044         308.3       0.3004       0.2394         308.4       0.208±0.004       0.06820±0.015         308.4       0.3004       0.2394         308.4       0.3064       0.2394         308.4       0.3004       0.2382±0.0036         312.3 ± 0.5       0.3660±0.0131       0.2974±0.0194         312.4 ± 0.4       0.2974±0.0194       0.2382±0.0036         312.4 ± 0.4       0.2974±0.0194       0.00608±0.0015         317.3 ± 0.4       0.3456       0.3313±00163         318.4       0.3456       0.3974±0.0191         318.4       0.3978±0.0091       0.3532±0.0161         322.2 ± 0.4       0.3978±0.0091       0.3974±0.00430         323.2 ± 0.4       0.3978±0.0091       0.3974±0.0018         327.3 ± 0.4       0.4022       0.327	298.2± 0.4			0.2267±0.0107				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	298.6 ± 0.9						0.0518±0.0008	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	298.7							0.0428
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	298.9 + 0.5					0.1825+0.0024		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	302.8 + 0.3					0.1020201002	0.0663+0.0011	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$302.9 \pm 0.5$					0 2028+0 0094	0.000010.0011	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$302.0 \pm 0.0$	0 2710+0 0154				0.202010.0004		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	303.0 ± 0.2	0.271010.0134		0 2561+0 0057				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$307.2 \pm 0.4$			0.230110.0037		0 2244±0 0080		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$307.7 \pm 0.3$	0 2054+0 0056				0.2244±0.0000	0 0020+0 0015	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$307.0 \pm 0.3$	0.3034±0.0030		0 0771 0 0044			0.0620±0.0015	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	308.2± 0.4		0.0004	0.2771±0.0044				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	308.3		0.3004		0.0004			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	308.4				0.2394			0.054
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	308.7	0.0000.0.0404						0.054
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$312.3 \pm 0.5$	0.3260±0.0131				0.0000.0.0000		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$312.4 \pm 0.4$					0.2382±0.0036	0.0000.00045	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$312.7 \pm 0.4$			0.0074.0.0404			0.0808±0.0015	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	313.2± 0.4			0.2974±0.0194				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	317.1 ± 0.3	0.3463±0.0075						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	317.3 ± 0.9					0.2578±0.0099		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	317.7 ± 0.1						0.0769±0.0010	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	317.8		0.3456					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	318.2± 0.4			0.3313±00163				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	318.4							0.0691
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	318.9				0.2905			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	321.6 ± 0.8	0.3712±0.0191						
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	322.2 ± 0.4						0.0904±0.0009	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	322.7 ± 0.6					0.2954±0.0430		
326.1 ± 0.3 0.3978±0.0091 327.3 ± 0.4 0.0941±0.0018 327.4 ± 0.3 0.4022 328.2± 0.4 0.3775±0.0116 0.0941±0.0018 0.3279±0.0086	323.2± 0.4			0.3532±0.0161				
327.3 ± 0.4     0.0941±0.0018       327.4 ± 0.3     0.3279±0.0086       327.8     0.4022       328.2± 0.4     0.3775±0.0116	326.1 ± 0.3	0.3978±0.0091						
327.4 ± 0.3 327.8 0.4022 328.2± 0.4 0.3775±0.0116	$327.3 \pm 0.4$						0.0941±0.0018	
327.8 0.4022 328.2± 0.4 0.3775±0.0116	327.4 ± 0.3					0.3279±0.0086		
328.2± 0.4 0.3775±0.0116	327.8		0.4022					
	328.2± 0.4			0.3775±0.0116				
328.2 0.344 0.0871	328.2				0.344			0.0871
329.5 ± 1.6 0.4172±0.0200	329.5 ± 1.6	0.4172±0.0200						
331.1 ± 0.6 0.1091±0.0043	331.1 ± 0.6						0.1091±0.0043	
332.1 ± 0.4 0.3554±0.0217	332.1 ± 0.4					0.3554±0.0217		
333.2± 0.4 0.4133±0.0014	333.2± 0.4			0.4133±0.0014				
0.3993	337				0.3993			
337.1 0.4519	337.1		0.4519					
338.6 0.115	338.6							0.115

It is noticeable that the solubility of urea in a mixture of ethanol and water increases with increasing temperature and decreases with increasing ethanol concentration to the mixture. The fact that the solubility decreases with decreasing temperature at low pressures is attributed to the reduction in density [19]. Figure 2 shows the decrease in solubility of urea with increasing mole fraction of ethanol in the solution. We can also observe that the standard deviation was low in all cases (about 4.7%). Figure 3 shows solubility data for urea in mixture of ethanol and water obtained in this study, along with the data of Lee and Lahti [13]. Comparing the data obtained in this study with the data provided by literature, the results were consistent.



Figure 2. Solubility of urea (in mole fraction) in all temperatures.



**Figure 3.** Solubility of urea: ( $\circ$ ), 20.2% ethanol; ( $\bullet$ ), 26.64% ethanol (Lee and Lahti); ( $\diamond$ ), 40.4% ethanol; ( $\bullet$ ), 53.36% ethanol (Lee and Lahti); ( $\Box$ ), 60.6% ethanol; (+), 100% ethanol; ( $\bullet$ ), 100% ethanol (Lee and Lahti).

#### Adjustments of solubility

Literature [13, 20, 21, 22] reports several equations or models to correlate solubility data. In this paper, we can cite the useful correlations proposed by Lee and Lahti [13], Yaws *et al.* [20], Buchowski *et al.* [22]. The solubility of urea in mixture of solvents was correlated by Eqs. (2), (3) and (4).

$$\ln x_{c1} = A + BT \tag{2}$$

where  $x_{c1}$  represents the solubility calculated using the Lee and Lahti equation; *A* and *B* represent the parameters of the equation and *T* represents the temperature measured in Kelvin.

$$\log x_{c2} = A' + \frac{B'}{T} + \frac{C'}{T^2}$$
(3)

where  $x_{c2}$  represents the solubility calculated using the Yaws equation; *A'*, *B'* and *C'* represent the parameters of the equation and *T* represents the temperature measured in Kelvin.

$$\ln\left[1 + \lambda\left(\frac{1 - x_{c3}}{x_{c3}}\right)\right] = \lambda h\left[\frac{1}{T} - \frac{1}{T_m}\right]$$
(4)

where  $x_{c3}$  is the solubility of urea calculated using the Buschowski equation;  $\lambda$  and h are the model parameters, T and  $T_m$  are the experimental and the standard melting point of urea in Kelvin, respectively.

The correlations of experimental data and data calculated using the thermodynamic models obtained from the relative deviation (RD) expressed by Equation 5 are listed in Table 2. The parameters of models obtained from linear and nonlinear regressions and their values are listed in Tables 3–4. The relative average deviation (RAD) and the corresponding root mean square deviation (RMSD) along with the R<sup>2</sup> as expressed by eqs 5–7 are shown in Tables 3–5.

$$RD = \frac{x_i - x_{ci}}{x_i} \tag{5}$$

$$RAD = \frac{1}{N} \sum_{i=1}^{N} \left| \frac{x_i - x_{ci}}{x_i} \right|$$
(6)

$$RMSD = \left[\frac{1}{N}\sum_{i=1}^{N} \left|\frac{x_i - x_{ci}}{x_i}\right|\right]^{\frac{1}{2}}$$
(7)

Table 2 shows the experimental and calculated results of solubility for urea in ethanol+water and in pure ethanol using the Equations 2 - 4. It is important to comment that to calculate the values in Table 2 it was follow the same experimental temperatures showed in Table 1.

According to the above-mentioned correlations of experimental data obtained at different temperatures in various mixtures of ethanol and water and in pure ethanol together with the calculated data (Tables 2-5), it was indicated that the solubility of urea calculated from the studied models showed good agreement. Taking the solubility data in the selected solvents fitted by the Yaws et al. model as an illustration, the relative average deviations are 0.01%, 0.06%, 0.16%, and 0.62%, respectively; which indicate that the modified Yaws et al. equation is suitable for correlating the solubility data of urea in the mixtures of ethanol and water and in pure ethanol. The same conclusion can be drawn after analyzing the solubility data and the parameters that fitted by the Lee and Lahti equation and the Buchowski λh equation.

However, we can see that the RAD values of Lee and Lahti equation, the Yaws *et al.* equation and the Buchowski–Ksiazaczak  $\lambda$ h equation are 4.84%, 0.86%, and 0.97%.

This result indicates that the Yaws *et al.* model proved to be more accurate and suitable for the description of dissolution of urea in the studied solvents at various temperatures.

Figure 4 shows the solubility of urea in a mixture of ethanol and water and in pure ethanol correlated with Equation (3). Analyzing Figure 4, it can be noted that the equation proposed by Yaws *et al.* (Equation 3) correlates the solubility of urea data well.

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т /к	x1	Lee and Lahti model Eq. 2	Yaws model Eq. 3	Buchowski <i>λh</i> model Eq. 4	т /к	x1	Lee and Lahti model Eq. 2	Yaws model Eq. 3	Buchowski <i>λh</i> model Eq. 4
		0.901of e	thanol				0.3757 of e	ethanol	
279.9	0.1779	0.1890	0.1782	0.17667	280.7	0.1128	0.1195	0.1125	0.1104
285.3	0.2007	0.2061	0.2002	0.19971	286.6	0.1252	0.1357	0.1316	0.1311
289.4	0.2161	0.2201	0.2176	0.21766	288.9	0.1486	0.1426	0.1397	0.1396
293.9	0.2392	0.2367	0.2374	0.23781	294.5	0.1485	0.1608	0.1605	0.1615
297.9	0.2600	0.2524	0.2556	0.25610	298.9	0.1825	0.1767	0.1783	0.1798
303.0	0.2710	0.2739	0.2794	0.27993	302.9	0.2028	0.1926	0.1956	0.1973
307.8	0.3054	0.2959	0.3024	0.30285	307.7	0.2244	0.2135	0.2177	0.2194
312.3	0.3260	0.3181	0.3245	0.32478	312.4	0.2382	0.2362	0.2408	0.2423
317.1	0.3463	0.3436	0.3485	0.34860	317.3	0.2578	0.2625	0.2666	0.2673
321.6	0.3712	0.3694	0.3714	0.37133	322.7	0.2954	0.2948	0.2969	0.2965
326.1	0.3978	0.3972	0.3945	0.39443	327.4	0.3279	0.3261	0.3249	0.3231
330.8	0.4172	0.4283	0.4190	0.41894	332.1	0.3554	0.3608	0.3546	0.3510
0.2096 of ethanol							1.0000 of	etanol	
278.1	0.1503	0.1639	0.1572	0.1476	279.7	0.0277	0.0341	0.0256	0.0239
283.1	0.1809	0.1784	0.1742	0.1688	283.9	0.0325	0.0375	0.0313	0.0312
288.1	0.1956	0.1942	0.1923	0.1905	288.7	0.0353	0.0419	0.0385	0.0394
293.1	0.2127	0.2115	0.2117	0.2127	293.5	0.0406	0.0467	0.0462	0.0474
298.1	0.2267	0.2302	0.2322	0.2354	298.6	0.0518	0.0525	0.0548	0.0557
303.1	0.2561	0.2506	0.2540	0.2585	302.8	0.0663	0.0578	0.0620	0.0624
308.1	0.2771	0.2728	0.2770	0.2820	307.8	0.0820	0.0648	0.0705	0.0702
313.1	0.2974	0.2970	0.3012	0.3059	312.7	0.0808	0.0725	0.0785	0.0776
318.1	0.3313	0.3233	0.3267	0.3303	317.6	0.0769	0.0811	0.0860	0.0849
323.1	0.3532	0.3519	0.3535	0.3550	322.2	0.0904	0.0901	0.0925	0.0916
328.1	0.3775	0.3831	0.3815	0.3800	327.3	0.0941	0.1013	0.0988	0.0988
333.1	0.4133	0.4170	0.4108	0.4054	331.1	0.1091	0.1105	0.1029	0.1041

Table 2. Experimental and calculated (Eq. 2 - 4) solubility of urea in pure ethanol and ethanol+water mixtures.

 Table 3. Parameters of the Lee and Lahti model for Urea in pure ethanol and ethanol+water mixtures.

Solvents	Α	В	RAD	RMSD	
0.901% of ethanol	-616.646	0.01608	0.0030	0.0547	
0.2096% of ethanol	-652.989	0.01698	0.0031	0.0555	
0.3757% of ethanol	-815.816	0.02150	0.0060	0.0778	
1.0000% of ethanol	-978.054	0.02289	0.0363	0.1905	
		∑(RAD) =0.0484			

Table 4. Parameters of the Yaws model for Urea in pure ethanol and ethanol+water mixtures.

Solvents	A'	B'	C'	RAD	RMSD	
0.901% of ethanol	0.000	311.0	-149600.0	0.0001	0.0099	
0.2096% of ethanol	1.724	-702.9	-67.335	0.0006	0.0246	
0.3757% of ethanol	1.700	-555.7	-52984.7	0.0016	0.0405	
1.0000% of ethanol	-10.00	6395.0	-1134645.0	0.0062	0.0790	
			∑(RAD) = 0.0086			



Figure 4. Mole fraction solubility of urea: (○), 20.2% ethanol; (□), 40.4% ethanol; (◊), 60.6% ethanol; (▲), 100% ethanol; (-) correlated data with Equation (3)

**Table 5.** Parameters of the Bucchowski *λh* model for Urea in pure ethanol and ethanol+water mixtures.

Solvents	λ	h	RAD	RMSD
0.901 of ethanol	-0.853	1191.074	0.0002	0.0127
0.2096 of ethanol	-0.803	1172.048	0.0023	0.0477
0.3757% of ethanol	-0.952	1761.671	0.0017	0.0413
1.0000% of ethanol	-0.192	862.233	0.0056	0.0748
		∑(RAD) = 0.0097		

## Conclusion

The solubility of urea in ethanol-water mixtures and in pure ethanol within the temperature range 278.1 to 333.1K was measured. The authors got the following conclusions: (1) The solubility of urea increased when temperature increased. (2) The addition of ethanol in the mixture resulted in a decreasing of urea solubility which can be verified by analyzing the experimental data of this paper and the literature data. (3) The solubility phenomena of urea were evaluated using the thermodynamics models. The data calculated from the Yaws *et al.* model was in good agreement with the experiment. This model was the most suitable for the description of the dissolution of urea.

Also, the experimental apparatus proved to be efficient in determining the data solubility using the gravimetric method, since the standard deviations of the samples were low.

The solubility data obtained in this paper is important because it may also contribute to other

scientific research, since there are references where the solubility of urea in solution and it behavior influence and modify the system under study.

## List of symbols

- *A* Parameter of Equation 2
- *A'* Parameter of Equation 3
- *B* Parameter of Equation 2
- *B*' Parameter of Equation 2
- C' Parameter of Equation 3
- *h* Parameter of Equation 4
- $\lambda$  Parameter of Equation 4
- m, Mass
- *M*<sub>i</sub> Molecular weight
- N Number of experiments in Equation 6
- T Temperature [K]

- Experimental urea solubility [mole
- x<sub>exp</sub> fraction]
- $x_{c1}$  Calculated solubility using Equation 2
- $x_{c2}$  Calculated solubility using Equation 3
- $x_{c3}$  Calculated solubility using Equation 4
- △ Standard deviation

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## References

- Violaki K, Mihalopoulos N. Urea: An important piece of Water Soluble Organic Nitrogen (WSON) over the Eastern Mediterranean Science of Total Environment. 2011;409:4796-801.
- [2] Voskov AL, Babkina TS, Kuznetsov AV, Uspenskaya IA. Phase Equilibria in the Urea— Biuret—Water System. J. Chem. Eng. Data. 2012;57(11):3225-32.
- [3] Glibert PM, Trice TM, Michael B, Lane L. Urea in the tributaries of the Chesapeake and coastal bays of Maryland Water Air Soil Pollut. 2005;160:229–43.
- [4] Francis PS, Lewis SW, Lim KF. Analytical methodology for the determination of urea: current practice and future Anal. Chem. 2002;21:389–400.
- [5] Józwiak M, Tyczynska M, Bald A. Viscosity of Urea in the Mixture of N,N-Dimethylformamide and Water. J. Chem. Eng. Data. 2013;58(2):217-24.
- [6] Hu Y, Chen X, Yang W, Guan J. Measurement and correlation of urea I-tartaric acid in aqueous ethanol solution. Thermochimica Acta. 2009;484: 38-40.
- [7] Lim J, Jang S, Cho HK, Shin MS, Kim H. Solubility of salicylic acid in pure alcohols at different temperatures J. Chem. Thermodynamics. 2013;57:295-300.
- [8] Tang J, Mu R, Zang B. Fan X. Solubility of urea phosphate in water + phosphoric acid from (277.00 to 354.50)K. J. Chem. Eng. Data. 2007;52:1179-181.
- [9] Loeser E, DelaCruz M, Madappalli V. Solubility of Urea in Acetonitrile—Water Mixtures and Liquid—Liquid Phase Separation of Urea-

Saturated Acetonitrile—Water Mixtures. J. Chem. Eng. Data. 2011;56(6):2909-13.

- [10] Oliveira MLN, Malagoni RA, Franco Júnior MR. Fluid Phase Equilibria. Solubility of citric acid in water, ethanol, n-propanol and in mixtures of ethanol + water. 2013;352:110-13.
- [11] Oliveira MLN, Malagoni RA, Fehr M, Franco Júnior MR. Obtaining Solubility Data from a Liquid-Liquid Equilibrium Cell. Chem. Eng. Comm. 2008;195:1076-084.
- [12] Wang Q, Xu H, Li X. Solubilities of Terephthalic Acid, Phthalic Acid, and Isophthalic Acid in Tetrahydrofuran, Cyclohexanone, 1,2-Diethoxyethane, and Acetophenone J. Chem. Eng. Data. 2009;54(11):3130-132.
- [13] Lee FM, Lahti LE. Solubility of urea in wateralcohol mixtures. J. Chem. Eng. Data. 1972;17(3)304-06.
- [14] Lee FM, Lahti LE, Stoops CE. Solution properties of urea-alcohol-water mixtures. J. Chem. Eng. Data. 1976;21(1):36-40.
- [15] Prausnitz JM, Lichtenthaler RN, de Azevedo EG. Molecular Thermodynamics of Fluid Phase Equilibria. Third edition. Prentice Hall International Series in the Physical and Chemical Engineering Sciences, 1999.
- [16] Ran Y, He Y, Yang G, Johnson JLH, Yalkowosky SH. Estimation of aqueous solubility of organics compounds by using the general solubility equation. Chemosphere 2002;48:487-509.
- [17] Bernardes EA, Brunetto RS, Franco Jr MR. In: 15th COBEQ – Congresso Brasileiro de Engenharia Química, 2004, Curitiba/Brazil. Proceedings of the 15th COBEQ, 2004. p. 1-8.
- [18] Orbey H, Sandler SI. Relative measurements of activity coefficients at infinite dilution by gas chromatography. Ind. Eng. Chem. Res.1991;30(8):2006-011.
- [19] Reddy SN, Madras G. Mixture solubilities of nitrobenzoic acid isomers in supercritical carbon dioxide. Journal of Supercritical Fluids. 2012;70:66-74.
- [20] Yaws CL, Lin X, Bu L. The water solubility of naphtenes Chem. Eng. 1994;101:119-28.
- [21]Yaws CL, Pan X, Lin X. Water Solubility Data for 151 Hydrocarbons. Chem. Eng.1993;100:108-11.
- [22] Buchowski H, Ksiazczak A, Pietrzyk S. Solvent activity along a saturation line and solubility of Hydrogen-Bonding solids. J. Phys. Chem. 1980;84:975-79.