

Calculation of thermodynamic and transport properties for systems containing liquid urea

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Abstract The worldwide demographic increase over the centuries has provided the development of new technologies for food production, among them including nitrogenous compounds adopted, such as urea. In industrial urea synthesis plants, it is essential that for the behavior of systems and equipment describe adopt models that calculate Thermodynamic and Transport Phenomena Properties (TTP). However, this task is not trivial since there is no agreement in the literature on the best models to describe this system. Therefore, this paper aims to get the correlations for the calculation of TTP for systems containing urea in liquid phase. To reach this goal, a survey of the models used in the literature was carried out. When the availability of these models was not observed, a regression of experimental data was carried out with the consequent formulation of empirical correlations for the system. In addition, the proposed models were validated with experimental and process data granted by FAFEN-BA. All correlations proposed in the work represented the system satisfactorily. The calculated data showed an average deviation of less than 4% to the real data. These findings might be useful for equipment design, flowsheet simulations and large-scale simultaneous optimization problems.

Keywords: Urea, Properties, Correlations, Models.

1 Introduction

Factors, such as the worldwide demographic increase over the centuries and the production of biofuels from agriculture as an alternative source of energy, have resulted in the growth of food production. Thus, technologies aiming to increase the productivity of food and raw materials have been studied all over the world. In this sense, use of industrial fertilizers has become a reality and they take on a relevant role in the agro-industrial sector. In addition, they are essential for efficient production in order to meet market demands. The main factories producing nitrogen fertilizers in Brazil are located in the northeast of the country, in the states of Bahia, FAFEN - BA and Sergipe, FAFEN - SE. FAFEN, at the Camaçari Petrochemical Complex in Bahia, has six stages in its urea production process: synthesis, purification/decomposition, vacuum concentration, pearlation, gas recovery/absorption, condensate treatment (BRITO, 2016).

In the engineering of processes and projects, the use of models to describe the behavior of systems and equipment is essential, since it is not always possible to get experimental data under operating conditions. However, due to the complexity and peculiarity of certain systems / equipments, commercial simulators do not always have models capable of describing these systems in their computational packages. In this context, the urea production process has been the motivation for several studies in modeling and process simulation. Bearing in mind that it presents a series of peculiar equipment beyond the electrolytic character of the solution that circulates in the equipment. In this sense, the calculation of properties such as: specific mass, viscosity, thermal conductivity and diffusivity of this system are fundamental in the process simulation, considering that it is necessary to know these for the sizing and design of equipment for the production of urea. Due to the complexity of the system, models for calculating these properties are not trivial and represent a significant contribution to literature, as well as to the fertilizer producing industries in question.

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Therefore, the aim of this paper is to get the correlations for the calculation of the Thermodynamic and Transport Phenomena Properties (TTP) for systems containing urea in liquid phase, providing an innovative approach in the representation of the system, since nothing was found in literature aggregating all of these properties. A contribution of this article, therefore, is to propose correlations not yet found in literature. In addition, make available, both for literature and for the industry, models for the calculation of the TTP that could be used in several applications such as assistance in equipment sizing and quality control.

2 Models and Correlations

Correlations that calculate Thermodynamic and Transport Phenomena Properties (TTP) with precision, reliability and simplicity are essential in process modeling, since they play a fundamental role in the representativeness of the models. To guide the research, the steps shown in Figure 1 were performed.

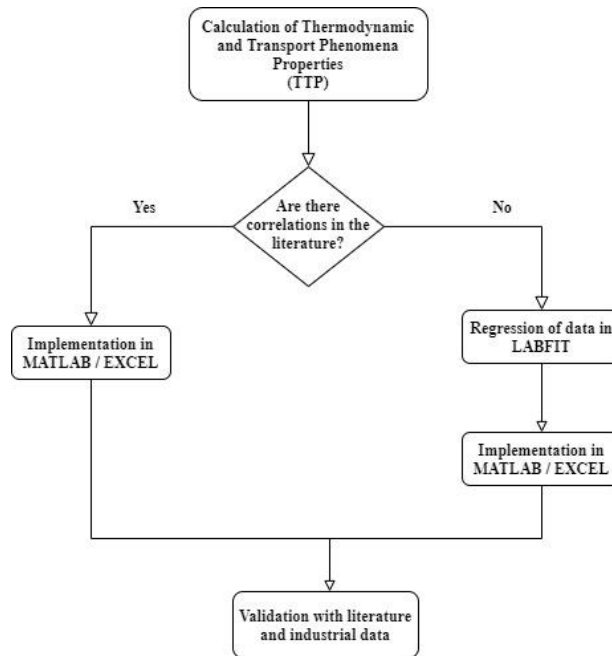


Fig. 1 Flowchart describing the procedure followed during the research

Therefore, this work applies models found in the literature and correlations obtained through experimental data to calculate specific mass, viscosity, diffusivity and thermal conductivity for the urea system in the liquid phase.

2.1 Specific mass

Specific mass is essential to characterize substances and mixtures. Calculating this property is indispensable for studying transport phenomena. In fluid mechanics, such as, the Reynolds dimensionless number allows to evaluate the type of flow (the stability of the flow) and can show whether it flows in a laminar or turbulent form, is a function of the specific mass. Thus, the precise calculation of this property is indispensable in the modeling and simulation of processes. Therefore, aiming to obtain an empirical correlation for the determination of the specific mass of urea in liquid phase, 46 experimental data by Brown (2006), Motin et al. (2002), Bhagwat; Mandloi (1946) in the temperature range of 278.15K to 368.97K and a regression was performed using the *LabFit* software and Equation 1 was found.

$$\rho_M = \frac{3.04 + x_{urea}}{0.2149 \cdot 10^{-2} - 0.2246 \cdot 10^{-5} \cdot T} - 3.545 \cdot T \quad (1)$$

where, ρ_M is the specific mass of the mixture given in kg/cm^3 , T is the temperature given in K, and x_{urea} is the molar fraction of urea.

2.2 Viscosity

Urea production process uses pumps in order to transport the product within the equipment system, therefore, it becomes extremely essential to know the viscosity of the solution at each stage of the process, assuring an effective pumping of the product. In addition to this, precise determination of viscosity is fundamental in the calculation of dimensionless numbers, such as Reynolds number (mentioned above) and Prandtl number. The latter, in heat transfer problems, controls the relative thickness of the moment and thermal limit layers, essential for calculating simultaneous heat and mass transfer coefficients.

Therefore, using 18 experimental data by Motin et al. (2002), expressed in the temperature range of 308K to 328K with a pressure of 1.01325 bar, a regression was performed using the LabFit software. Through this, a correlation was found in which it is possible to estimate the viscosity of aqueous urea as function of the molar fraction of urea in the solution and in the temperature, expressed in Equation 2.

$$\eta = 2.411 \cdot 10^{10} \cdot 18.93^{X_{Urea}} \cdot T^{(-5.432)} - 1.652 \cdot 10^{-5} \quad (2)$$

where, X_{Urea} is molar fraction of urea in the solution and T the temperature in K.

Furthermore, to help calculate the diffusivity, it was necessary to find a model that represents the relative viscosity of the system. Thus, Kawahara and Tanford (1966) proposed Equation 3 for aqueous solutions of urea at 25°C.

$$\frac{\eta}{\eta_0} = 1 + 3.75 \times 10^{-2} C + 3.15 \times 10^{-3} C^2 + 3.10 \times 10^{-4} C^3 \quad (3)$$

where, C is the concentration of urea in mol/L , η the viscosity of the solution and η_0 is the viscosity of the water at the same temperature as the solution.

2.3 Diffusivity

Diffusivity reflects the mass transfer dynamics of a system. This is used to calculate the mass flow, where the model proposed by Fick's law is typically used (LEIDENS et al., 2016). In addition, knowledge of this property is indispensable for calculating the non-dimensional Schmidt's number, defined as the ratio of moment diffusivity (viscosity) and mass diffusivity, and used to characterize fluid flows in which moment and mass diffusion processes exist simultaneously. In the production process of urea, it is extremely important to determine this property, since, in many equipments, such as absorption towers, mass transfer occurs between the liquid and gaseous phases. So, Gosting and Akeley (1952) propose the Gordon Equation for the calculation of urea diffusivity in water (Equation 4)

$$D = D_o \frac{\left[1 + C \frac{\partial \ln \gamma}{\partial C} \right]}{\frac{\eta}{\eta_0}} \quad (4)$$

where, D is the diffusivity of the mixture in cm^2/s , D_o is the limit value of the diffusivity when the concentration (C) tends to zero, γ is the activity coefficient and the term $\frac{\eta}{\eta_0}$ is the relative viscosity (presented in the previous item) which can be found for the urea system in water at 25°C by Equation 3.

2.4 Thermal Conductivity

The ability of a material to send heat characterizes the thermal conductivity property (PARK; ALONSO; NUNES, 1999). In the substance separation equipment, used on the production process of urea synthesis, simultaneous heat and mass transfer occurs. Thus, to represent this heat and mass exchange dynamics the calculation of specific properties, such as thermal conductivity, is required. The determination of this property is important to find the heat transfer coefficient, using the Prandtl coefficient. Therefore, Filippov (1968) proposes Equation 5 to calculate the thermal conductivity of mixtures in the liquid phase as a function of concentration.

$$k = k_{urea}x_{urea} + k_{H_2O}x_{H_2O} - \lambda x_{urea}x_{H_2O}|k_{H_2O} - k_{urea}| \quad (5)$$

where k is the thermal conductivity of the solution in W/mK, k_{urea} is the thermal conductivity of urea in W/m K, k_{H_2O} is the thermal conductivity of pure water in W/m K, x_{urea} is the molar fraction of urea, x_{H_2O} is the molar fraction of pure water and, finally, λ is a coefficient that depends on the substances in the solution.

3 Results and Discussion

This section aims to show the validation of the models for the transport and thermodynamic properties presented in the Section 2. Besides that, an analysis of the properties' behavior is performed.

3.1 Specific mass

Figure 2 represents experimental data by Brown et al. (2006), Motin et al. (2002) and results simulated by Equation 1 (empirical correlation obtained by regression of experimental data) of the specific mass variation for aqueous urea as a function of the urea concentration at a temperature of 283.15 K (Figure 2a), 308 K (Figure 2b) and 318 K (Figure 2c).

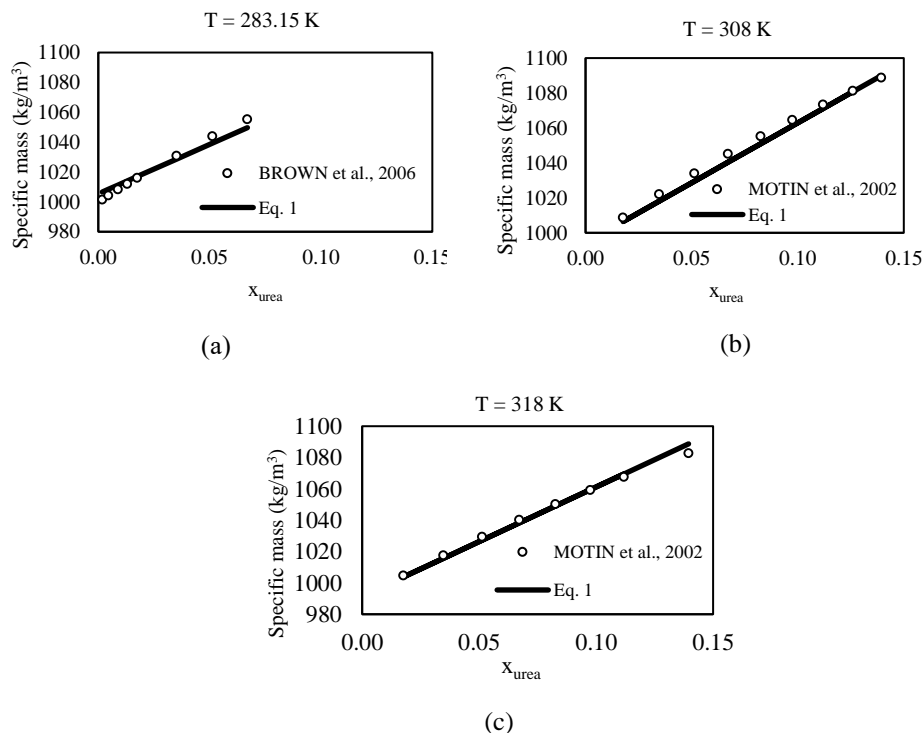


Fig. 2 Experimental and calculated data (Eq. 1) of specific mass of the urea and water system (a) temperature 283.15 K. (b) temperature 308.15 K. (c) temperature 318 K

Equation 1 represents the system satisfactorily in the indicated temperature range, since the average deviation between experimental data and calculated data was less than 1%. In addition, when the system temperature increases, the specific mass decreases, this is due to the property being inversely proportional to the volume, which in turn undergoes expansion with the increase in temperature, providing a decrease in specific mass. Furthermore, when increasing the concentration of urea in the system, the specific mass also undergoes an increase, expressed in the graph (b) of Figure 2. This occurs due to the increase in mass of the system, since the substance urea has a higher molecular weight than water. Besides that, Equation 1 was applied to industrial data from the FAFEN - BA urea production process, which compositions are shown in Table 1.

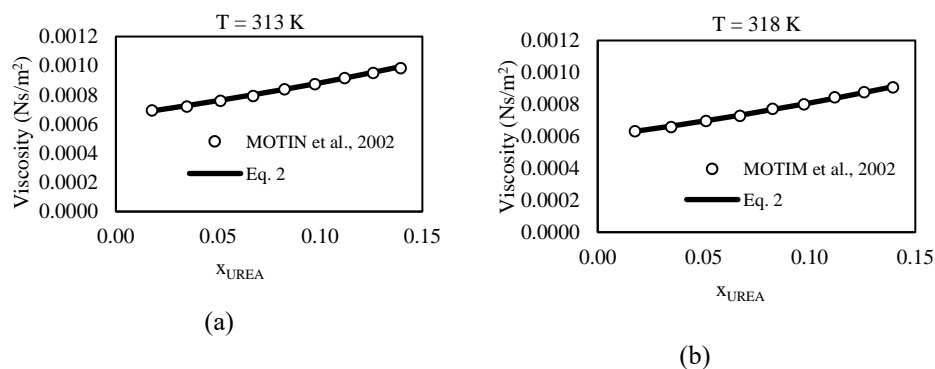
Table 1. Compositions of FAFEN - BA process streams and results

Temperature	Mass fraction	ρ_M (Kg/m ³) from FAFEN	Deviation of the ρ_M calculated by Eq. 1
429.15 K	$x_{NH_3} = 0.065, x_{CO_2} = 0.057$ $x_{H_2O} = 0.280, x_{CO(NH_2)_2} = 0.628$	0.88	2.3%
456.15 K	$x_{NH_3} = 0.327, x_{CO_2} = 0.099$ $x_{H_2O} = 0.132, x_{CO(NH_2)_2} = 0.440$	1	3.0%
469.15 K	$x_{NH_3} = 0.327, x_{CO_2} = 0.099$ $x_{H_2O} = 0.132, x_{CO(NH_2)_2} = 0.440$	0	6.5%

In Table 1, the process and calculated data were represented in a normalized manner, due to industrial confidentiality. Normalization was done using the following equation: $\rho_M = \frac{\rho - \rho_{Min}}{\rho_{Max} - \rho_{Min}}$. The average deviation between process and calculated data is less than 4%. Accordingly, it is possible to infer that, even with the presence of carbon dioxide and ammonia in the currents, the correlation found in Equation 1 satisfactorily characterizes the specific mass.

3.2 Viscosity

Figure 3 presents experimental data by Motin et al. (2002) and calculated by Equation 2 (empirical correlation obtained by regression of experimental data) for the viscosity property of the mixture as function of composition of urea at three different temperatures: 313 K, 318 K and 323 K.



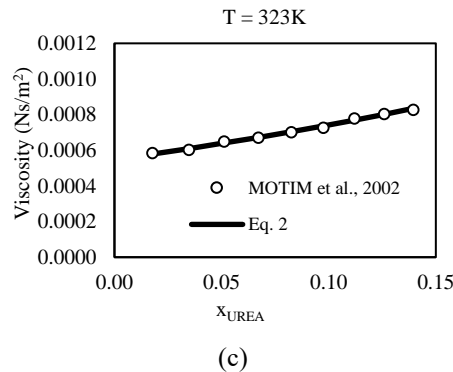


Fig. 3 Experimental and calculated data (Eq. 2) of specific mass of the urea and water system at pressure 1.01325 bar (a) temperature 313 K. (b) temperature 318 K. (c) temperature 323 K

Analyzing the results presented in Figure 3 and the average deviations below 1%, between the experimental and calculated data, it is possible to notice that Equation 2 is able to represent the viscosity for the studied system a very accurately displayed within pressure and temperature range applied. Furthermore, by increasing the system temperature, one can find that viscosity decreases. This is because the viscosity is directly proportional to the attraction force between the molecules. By increasing the temperature, the attraction force decreases, so, also decreases the viscosity. Brunetti (2008) presented this same finding.

As explained, in order to calculate diffusivity, it is necessary to know the relative viscosity of the system. Equation 3 was applied and the results were compared with experimental data, varying the concentration at 25°C. These results can be seen in Figure 4, where the relative viscosity curve as a function of the urea concentration is presented.

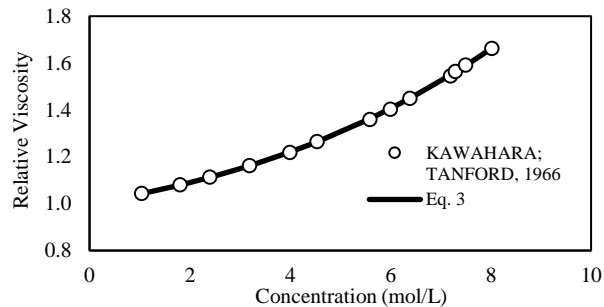


Fig. 4 Experimental and calculated data for the relative viscosity of the liquid phase of the urea system in water

Through the analysis of Figure 4, it can be observed that this correlation was validated for the calculation of viscosity with variation of concentration in the liquid phase of the urea and water system, since the average deviation found was less than 1%. In addition, it is noticed that by increasing the concentration of urea in the system, the viscosity also increases. This can be attributed, according to Brunetti (2008), to the increase of intermolecular forces with the increase of the concentration, causing a greater resistance to the flow fluid and, therefore, a higher viscosity.

3.3 Diffusivity

Figure 5 shows the validation of the Gordon Equation (Equation 4) for diffusion coefficient of the urea/water mixture. The experimental data are from Gosting and Akeley (1952) at 25°C.

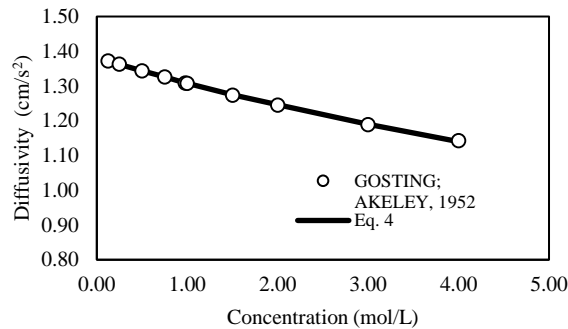


Fig. 5 Experimental diffusion coefficient (GOSTING; AKELEY, 1952) and calculated (Eq. 4) of the liquid phase of the aqueous urea system at 25°C

The semi-empirical Equation 4 from Gordon (1937) was initially proposed for application to the potassium chloride, sodium chloride and potassium nitrate systems in aqueous solution. However, as seen in Figure 5, the equation satisfactorily provides for other systems, such as urea in aqueous solution. Since, there is a low deviation between the experimental values of Gosting and Akeley (1952) and the one calculated by Equation 4, shown in the Figure 5. The deviations presented for each point in the chart are less than 0.3%. Therefore, it is possible to admit that Equation 4 predict satisfactory values for the diffusion coefficient of the urea system in water. Moreover, from the analysis of Figure 5, by increasing the concentration of urea the diffusion coefficient decreases. This happens because urea has an attractive interaction with water molecules, this, therefore, decreases the resistance of urea to move in water as the concentration increases (CREMASCO, 2002).

3.4 Thermal Conductivity

Equation 5 proposed by Filippov (1968) was used to calculate the thermal conductivity of the mixture of urea and water as function of molar fraction of urea at a constant temperature of 25 °C. Thermal conductivity curve as function of molar fraction of urea is expressed in Figure 6.

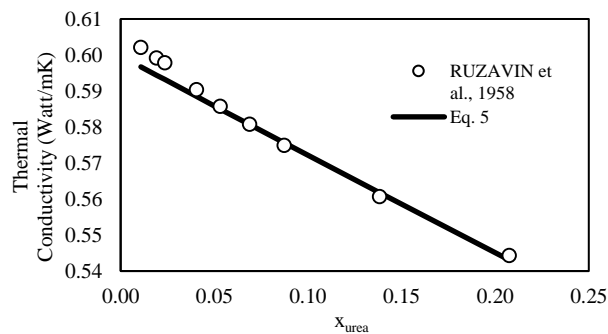


Fig. 6 Data from Ruzavin et al. (1958) and calculated (Eq. 5) for the thermal conductivity of the liquid phase of the aqueous urea system

From Figure 6, it is possible to infer that the mathematical model proposed by Filippov (1968), describes well the thermal conductivity for the aqueous urea system in the liquid phase, since it obtained an average deviation of less than 1% to the data of Ruzavin et al. (1958). Moreover, it is observed that by increasing the concentration of urea in the solution, thermal conductivity decreases. This is because urea is a molecular substance, which does not have free loads for heat conduction. Thus, by increasing the concentration of urea, the ability of the system to conduct heat decreases.

4 Conclusion

Results of the present work made it possible to obtain the correlations for the calculation of the Thermodynamic and Transport Phenomena Properties (TTP) for systems containing urea in liquid phase. In addition, it was also possible to understand the influence of some variables, such as temperature and concentration on the studied properties (specific mass, viscosity, diffusivity, and thermal conductivity). This is important to predict how properties under process conditions behave within an industrial urea synthesis plant. Furthermore, all the correlations proposed for the TTP were validated with experimental data and for the specific mass, also, with process data provided by FAFEN – BA, obtaining deviations of less than 4% between real and calculated data. Therefore, correlations can be used to represent the real system within the specified range of conditions. Correlations presented in this paper can be used to calculate the TTP for different applications in the industry and with contributions also in the literature.

5 References

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