

# MEASUREMENT OF VAPOR-LIQUID EQUILIBRIUM FOR ETHANOL-WATER-CALCIUM NITRATE AT NORMAL PRESSURE

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**ABSTRACT** – This paper aims to obtain experimental data on vapor-liquid equilibrium of the ethanol-water-calcium nitrate at atmospheric pressure, as well as the validation of the UNIFAC thermodynamic model. Several solvents have been studied to break the azeotrope of ethanol-water systems, including salts, organic solvents and ionic liquids. The choice of salt is due to the importance of searching for other cheaper solvents to separate ethanol from water. Thus, the data were measured using an Othmer-type ebulliometer and composition analysis was obtained using a digital densimeter. Salt was used at concentrations of 0.06 and 0.15 mole, and 30% (w/w) (dehydrated salt), to compare the behavior between the VLE with and without the salts. All the experiments were done in triplicate. An enrichment of ethanol in the vapor phase was observed, indicating the breaking of the azeotrope. Furthermore, the average relative deviation between the experimental measurements of calcium nitrate dehydrated 30% (w/w) and the predicted values by the model was less than 7% for the vapor phase composition and for the temperatures, therefore validating the model. This study showed that calcium nitrate is a solvent that can be used for the production of anhydrous ethanol with a high purity with low cost.

## 1. INTRODUCTION

The current higher energy demand is increasing the price of crude oil, affecting directly the global economic activity. These reasons have led to the development of researches that intend to find alternative, renewable, sustainable, efficient, low cost energy sources that release fewer contaminants and greenhouse effect gases. Among the many alternatives are the biofuels, an environmentally less aggressive energy source that is also an advantageous choice due to its recuperation, biodegradability and acceptable quality gas production capacity (Nigam & Singh, 2011).

In the past few years, anhydrous ethanol has evolved a great deal in the industrial market, mostly in the area of fuels, as a gasoline helper, allowing a high-octane fuel, which generates a superior consumption of the fuel, leading to a reduction in the CO and particulate emissions.

Brazil is second largest producer of ethanol of the world, using sugarcane as raw material. After removal of impurities and fermentation, it is generated a mixture of ethanol and water as product. Therefore, in order to obtain anhydrous ethanol, the mixture is required

to pass through a dehydration process. The presence of a minimum azeotrope in this system, around 89.4% ethanol composition at 351.35 K and atmospheric pressure, makes the separation could be more difficult (Kumar *et al.*, 2010). This azeotrope prevents the complete separation of ethanol through simple distillation under atmospheric pressure.

In general, the process most commonly used for the separation is the azeotropic or extractive distillation, depending on the volatility of the substance. The extractive distillation is based on the addition of a low volatility solvent at elevated concentrations, above the feeding and that it remains in contact with the liquid in the column. The objective is to increase the difference between the volatilities values of the components by improving the volatility of one of the components, making it possible to separate them. In the azeotropic distillation however, the solvent added is more volatile than the components of the mixture, being withdraw at the top of the column. The technology most used in the separation of water-ethanol mixtures is the extractive distillation, and its efficiency depends, more than anything else, on the extractive solvent used (Huang *et al.*, 2008).

Many solvents have been used in the extractive distillation as salts, glycerol and other organic solvents (Souza *et al.*, 2013). Due to this, the aim of this study is the measurement of vapor-liquid equilibrium data (VLE) of ethanol-water mixture with calcium nitrate at different concentrations. It will be possible to see if the salt is a potential solvent to be applied in an extractive distillation.

## **2. MATERIALS AND METHODS**

### **2.1. Materials**

Tetra-hydrated calcium nitrate (Vetec Química Fina Ltda, Rio de Janeiro, Brazil), dehydrated calcium nitrate, absolute ethanol (99.8% of minimum purity, Vetec Química Fina Ltda, Rio de Janeiro, Brazil) and distilled water were used to produce the solutions used in the work.

The thermophysical properties of ethanol and water, ensuring their purity, were previously measured and published in Souza *et al.* (2013).

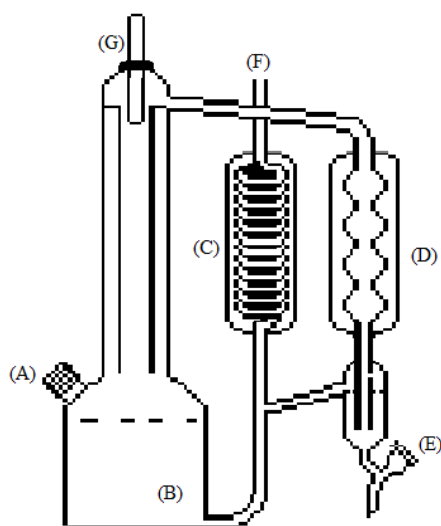
### **2.2. Experimental methodology**

The experimental data were measured using water-ethanol solutions with molar fractions of ethanol varying from 0.2 to 0.95 and tetra-hydrated calcium nitrate with concentrations of 0.06 and 0.15 mole, in a salt free basis. Dehydrated calcium nitrate was also used in a concentration of 30% (w/w), in a salt free basis. The composition of 0.06 mole was chosen to compare the data with others already published. The data at 0.15 mole concentration was used in order to find out the improve of the ethanol concentration in vapor phase. The measurements done with 30% (w/w) of concentration were studied to validate the thermodynamic model already used in Soares (2010).

The dehydrated calcium nitrate 30% (w/w) was obtained placing the hydrated salt in a glass vacuum desiccator connected to a vacuum pump (New Pump), where it stayed until 48 hours and it was observed a low variation of mass.

The experiments were performed in a glass Othmer type ebulliometer, as shown in Figure 1. This ebulliometer is made of one equilibrium cell, two condensers and two openings where samples of the liquid and vapor phases can be collected. The equilibrium cell's total volume is 300 mL, where the mixture filled approximately 50 mL. The experiments were done at atmospheric pressure conditions and in triplicate. The liquid and vapor phase temperatures were measured through digital thermometers with an uncertainty of 0.01 °C. After achieving equilibrium, a sample of the vapor phase is collected and analyzed in a digital densimeter, and the ethanol composition of the vapor phase is calculated according to the calibration curve that was constructed using different concentrations of ethanol-water solutions.

Figure 1 – Ebulliometer's schematic diagram (Adapted from Souza *et al.*, 2013).



(A) liquid phase temperature measurement, (B) equilibrium cell, (C) secondary condensador, (D) primary condensador, (E) vapor phase sample collection, (F) atmospheric air, (G) vapor phase temperature measurement

### 3. RESULTS AND DISCUSSION

Tables 1 and 2 present the VLE data of the ethanol-water-tetra hydrous calcium nitrate 0.06 mole and 0.15 mole respectively, both in salt free basis, measured in this paper, with the respective standard deviations of the measurements.

Table 1 – VLE data of the ethanol-water-tetra hydrous calcium nitrate 0.06 mole

x	y	T (°C)	SD*y	SD*T
0.2	0.6813	81.77	0.0351	0.7024
0.4	0.7713	80.57	0.0245	0.5508
0.6	0.7936	79.40	0.0111	0.2000
0.8	0.9132	78.97	0.0199	0.0577
0.9	0.9444	76.67	0.0035	0.5774
0.95	0.9480	74.87	0.0104	0.0577
*Standard deviation (SD)				

Table 2 –VLE data of the ethanol-water-tetra hydrous calcium nitrate (0.15 mole)

x	y	T (°C)	SD*y	SD*T
0.2	0.7189	80.40	0.0348	0.4583
0.4	0.7733	79.27	0.0220	0.6429
0.6	0.7955	78.90	0.0223	0.2646
0.8	0.8589	78.50	0.0094	0.2646
0.9	0.9111	78.30	0.0131	0.1732
0.95	0.9538	78.18	0.0305	0.1328
*Standard deviation (SD)				

In order to demonstrate the salt's efficiency in azeotrope breaking, Figure 2 presents the water-ethanol system's data (Dechema, 1981) and the data of the 0.06 and 0.15 mole series measured in this paper (presented in Tables 1 and 2), with the objective to compare the behaviors in azeotrope breaking at different concentrations.

Figure 2 – VLE data of ethanol-water binary system (Dechema, 1981) compared to measured data with 0.06 and 0.15 mole of calcium nitrate.

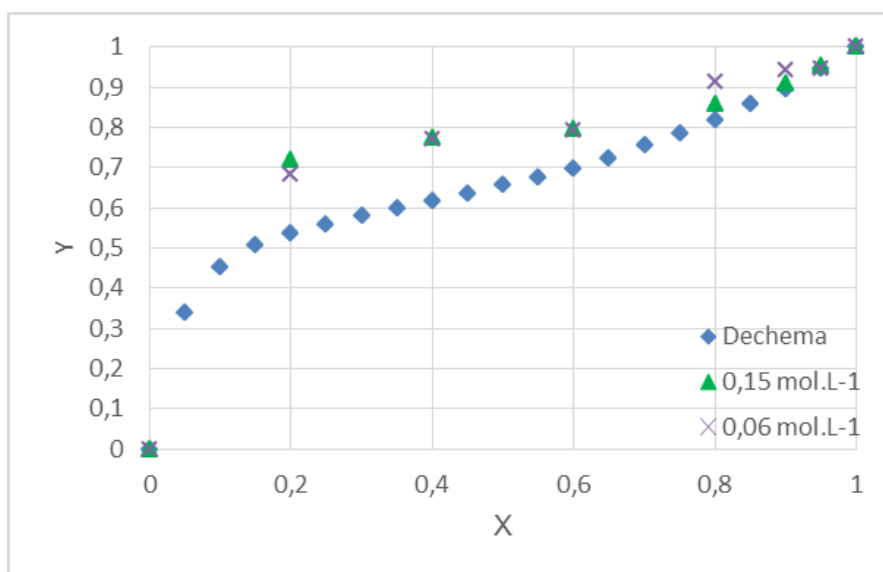
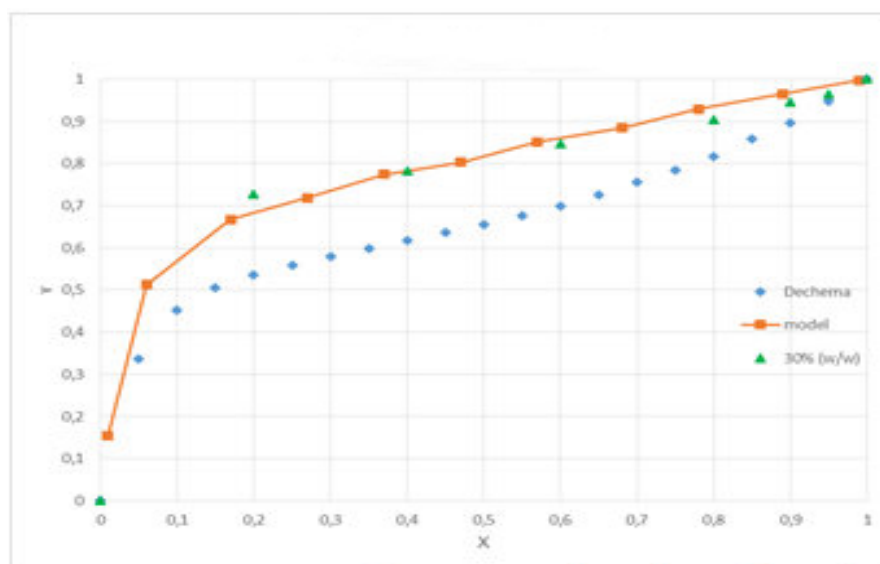


Table 3 presents the VLE data of ethanol-water-dehydrated calcium nitrate (30% w/w, in salt free basis), with the standard deviations of the measurements and relative deviations between the experimental and predicted values by the model used by Soares (2010). The values of deviations were very low, indicating the acceptable behavior of the model in the VLE prediction, as shown in Figure 3.

Table 3 – VLE data for the ternary system with 30% (w/w) of calcium nitrate

x	y	T (°C)	SD*y	SD*T	RD**y	RD**T
0.20	0.7271	81.40	0.0015	0.5519	0.0616	0.0218
0.40	0.7831	79.65	0.0146	0.0436	0.0006	0.0274
0.60	0.8465	79.10	0.0046	0.0500	0.0159	0.0253
0.80	0.9039	78.48	0.0017	0.1305	0.0350	0.0171
0.90	0.9459	78.44	0.0181	0.0252	0.0236	0.0142
0.95	0.9645	78.41	0.0083	0.0361	0.0204	0.0119
*Standard deviation (SD)				**Relative deviation (RD)		

Figure 3 – Measured and predicted VLE of ethanol-water-calcium nitrate 30% (w/w) data.



## 4. CONCLUSIONS

In this paper, original VLE data were measured of the water-ethanol-calcium nitrate ternary system at atmospheric pressure. An enrichment of ethanol in the vapor phase was observed for all the concentrations studied, thus breaking the azeotrope. It was also possible to validate the thermodynamic model proposed, due to the fact that the average relative deviations of temperature (2.74%) and ethanol composition in the vapor phase (6.16%) were low when compared to the experimental data.

## 5. REFERENCES

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