

# INFLUENCE OF THE SODIUM ACETATE ON THE VAPOR-LIQUID EQUILIBRIUM OF THE SYSTEM WATER-ETHANOL AT NORMAL PRESSURE

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**RESUMO** – This work aimed the evaluation of a saline extractive distillation for the ethanol production. Unlike the current method of dehydration of ethanol, which uses a solvent, distillation with the use of salt does not include problems related to toxicity and has lower power consumption, since salt is not volatilized within the distillation column. Many salts had been tested like calcium chloride, calcium nitrate and a mixture of sodium and potassium acetates, although vapor-liquid equilibrium data involving them are scarce in the literature. Other works proved that pure potassium acetate and the mixture of acetates can break the azeotrope, but there were not results involving pure sodium acetate. Due to that, in this work, vapor-liquid equilibrium data of the water-ethanol system with pure sodium acetate, at different concentrations, were measured in a Othmer type ebulliometer, at normal pressure. The data were measured at 10, 15 and 20% w/w and at 0.06 mol.L<sup>-1</sup>, to better understand the influence of the salt in the equilibrium behavior. Analysis of the vapor and liquid phases were done in a digital densimeter. The sodium acetate enriched vapor phase in ethanol concentration and lower quantities of the salt better influence the equilibrium. Higher quantities of salt did not have good results because the salt did not yet solubilize in the solution. The model well correlated the data measured with lower deviations in temperature (1.49%) and vapor phase concentration (1.95%).

## 1. INTRODUÇÃO

Distillation is one of the most important separation processes of liquid mixtures. There are systems, however, that cannot be separated by simple distillation, due to the similar boiling points of the components or by the presence of azeotropes. The water-ethanol mixture is one of the examples and due to that characteristic; it should add a third component able to modify the vapor-liquid equilibrium (VLE) relations of the system, as Soares (2010) shows in his work. In general, a solvent is added to the mixture and the distillation is called extractive or azeotropic, according to the component volatility, as Henley and Seader (1981) says.

Some salts can be effective in the VLE modification of this type of mixture, although the solvent in pure state can be solid or liquid. In contrast of the liquid solvents, salts are not volatile and consumed less energy throughout the process. Moreover, the toxicity of the liquid solvents has restricted their use in the extractive distillation. As Soares (2010) says in his work, in this context, it becomes increasingly important the development of saline extractive

distillation as a process alternative to the current processes which rely on the use of organic solvents.

Soares (2010) says that the modeling and simulation, as the unit project, need knowledge of some thermodynamic properties of the studied system. In the case of water-ethanol mixture, there are some works in the literature dealing with VLE data (Miró et al., 1962; Cook and Furter, 1968; Nishi, 1975; Vercher et al., 1991; Furter, 1992), but are still scarce data involving the same system with salts.

The ethanol dehydration process, proposed by Gorhan, employed a mixture of acetate salts (70% of potassium acetate and 30% of sodium acetate) that were easily treated in the distillation column as aqueous or alcoholic solutions of these salts, according to Furter (1992).

The feasibility of performing a saline extractive distillation has been criticized because of the possibility of the salt deposition inside the column, which is not correct. The salt is typically more soluble in the less volatile component than in the more volatile. As the less volatile component (water) is at a minimum concentration at the top reflux stream and gradually increases toward the bottom of the column, the salt concentration contained in descending liquid saturation decreases to increasingly lower levels, and therefore tend to remain at higher concentrations in the solution. Briefly, it can be stated that, although the concentration of the salt dissolved in the liquid phase remains relatively constant at each stage, its solubility increases steadily decreasing their degree of saturation progressively to the bottom of the column, according to Cook and Furter (1968).

Looking after the possibility to dehydrate ethanol with salts, Soares et al. (2014) studied the behavior of different salts in a raschig ring packed distillation column and proved that some salts had a similar influence on the VLE of the water-ethanol system. Sodium chloride, the mixture of potassium and sodium acetates and pure sodium acetate had the same influence enriching ethanol in the vapor phase 66% and calcium chloride (67%). Pure potassium acetate increased the concentration of ethanol in the vapor phase in 70% and calcium nitrate had the worse behavior (62%).

Although Soares et al. (2014) had work with different salts, only some of them had VLE data with ethanol-water system at constant concentrations: potassium acetate ( $0.06 \text{ mol.L}^{-1}$ ), according to Vercher et al. (1991); calcium chloride (16.7%w/w), according to Nishi (1975) and calcium nitrate (30 g of salt/100 g of solution), according to Miró et al. (1962).

Cook and Furter (1968) proved that potassium acetate can break the azeotrope of ethanol-water system, although the salt causes the appearance of very quantity of foam. Due to that, this work had as objective the measurement of VLE data, at normal pressure, of ethanol-water system with sodium acetate at different concentrations to compare the results with potassium acetate and with the mixture of acetates. Moreover, VLE data can prove that pure sodium acetate could be an ideal solvent to be applied in extractive distillation.

## **2. MATERIALS AND METHODS**

### **2.1. Experimental apparatus**

The experimental data were measured from water-ethanol mixtures varying the concentration from 0.2 to 0.95 of molar fraction of ethanol. The sodium acetate was added to the solution in four different proportions: 10, 15 and 20 (% w/w) and 0.06 molar. These concentrations of the salt were chosen because Soares (2010) had predicted new data for this system using a thermodynamic model for electrolytes, to compare the data.

The experiments were performed using an Othmer-type ebulliometer made of borosilicate glass, as Figure 1 shows. It was designed based on other works and well tested for other systems studied previously by Souza et al. (2013). It is composed by an equilibrium cell, two condensers and two sample ports to take the samples of vapor and liquid phases. Only the vapor phase is recirculated. The total volume of equilibrium cell is 300 cm<sup>3</sup> and about 100 cm<sup>3</sup> was occupied by the mixture. In the serpentine type condenser, there is an open point to the air, ensuring atmospheric pressure (1 atm). The temperatures of vapor and liquid phases were measured using thermometers with  $\pm 0.1$  °C of uncertainty. The experiments were done in triplicate.

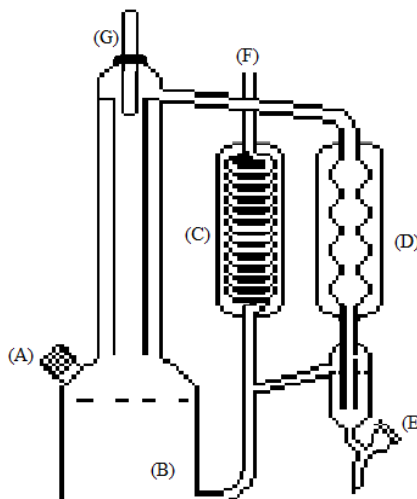


FIGURE 1 – Schematic diagram of the ebulliometer used in this work. (A) temperature measurement and sampling of liquid phase, (B) equilibrium cell, (C) secondary condenser, (D) primary condenser, (E) vapor phase sampling port, (F) open point to the air, (G) temperature measurement of vapor phase.

Before the equilibrium data experiments with the salts, water-ethanol (Soares, 2014) and water-ethanol-glycerol vapor-liquid equilibrium data (Souza et al., 2013) were measured in the same ebulliometer. with the objective to compare, to validate the methodology and to know the deviations of the measurements.

## 2.2. Sample analysis

Sample compositions were determined according to the same methodology applied by Soares et al. (2014).

## 2.3. Experimental Procedure

Experimental procedure starts by charging ethanol, water and pure sodium acetate into the equilibrium cell, according to ethanol-water composition mixtures and to the defined proportions of the salt. Small glass spheres were added to control the boiling and to assure the homogeneous heating. After beginning the circulation of water through the condensers, a heat source was turned on. The vapor phase temperature was measured every 10 min until it remains constant for 30 min, when it was assumed that steady state was reached, the temperature value was finally registered. At this moment, vapor samples were collected and analyzed using the digital densimeter (GEHAKA, DSL 920 model).

### 3. RESULTS AND DISCUSSION

#### 3.1. Experimental results

The experimental results of the vapor-liquid equilibrium (VLE) with sodium acetate at the four different concentrations were presented in the figures below. The results present in the figures represent the medium of results of each triplicate.

As Figure 2 shows, the experimental vapor-liquid equilibrium data for the binary system water-ethanol, studied by DECHEMA (1981) and ternary system water-ethanol-sodium acetate at 10% (w/w), 15% (w/w), 20% (w/w) and 0.06 mol.L<sup>-1</sup>, to investigate the saline influence on ethanol dehydration.

The VLE data measured with sodium acetate at the concentrations of 10% (w/w), 15% (w/w) and 20% (w/w), it can be observed that the azeotrope was not broken, although ethanol was enriched in the vapor phase.

Probably, this phenomenon occurred because of the large quantity of salt added into the equilibrium cell, that did not completely solubilize in the solution, causing deviations in the vapor concentration. Lower quantity of salt was used to test the behavior of the VLE.

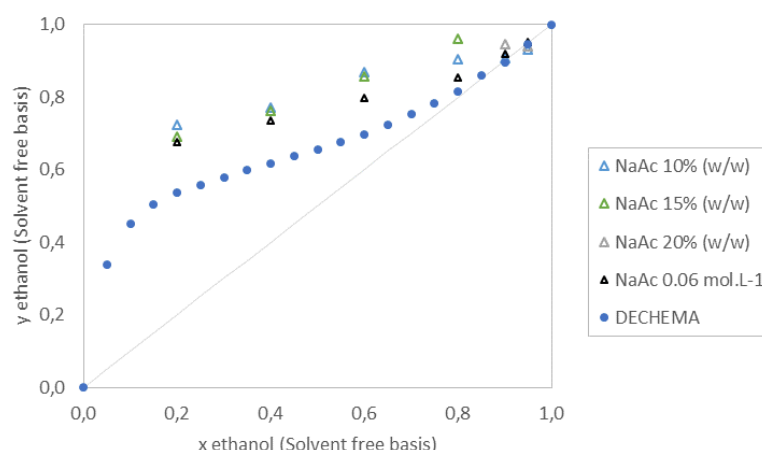


FIGURE 2 – Comparison between all VLE data for the ternary system water-ethanol-sodium acetate.

Table 1 shows all the experimental data for the four different concentrations of sodium acetate and Table 2 shows the standard deviation of the vapor composition and temperature measurements.

TABLE 1 – Experimental VLE for ethanol-water-sodium acetate, for the four different concentrations of 10, 15 and 20% (w/w) and 0.06 mol.L<sup>-1</sup>

X ethanol	10% (w/w)		15% (w/w)		20% (w/w)		0.06 mol.L <sup>-1</sup>	
	Y ethanol	T/K	Y ethanol	T/K	Y ethanol	T/K	Y ethanol	T/K
0.20	0.723	354.02	0.691	353.50			0.677	353.95
0.40	0.773	352.98	0.763	350.50			0.736	353.25
0.60	0.869	352.75	0.858	349.70			0.797	352.55
0.80	0.906	349.65	0.961	351.90			0.854	351.85
0.90	0.908	352.05			0.946	351.95	0.918	351.85
0.95	0.930	352.28			0.942	351.92	0.953	352.05

X ethanol – liquid composition of ethanol in solution – solvent free basis

Y ethanol – vapor composition of ethanol in equilibrium – solvent free basis

TABLE 2 – Standard deviations ( $\delta$ ) for the experimental VLE measurements, for ethanol-water-sodium acetate system

X ethanol	10% (w/w)		15% (w/w)		20% (w/w)		0.06 mol.L <sup>-1</sup>	
	$\delta$ Y ethanol	$\delta$ T/K	$\delta$ Y ethanol	$\delta$ T/K	$\delta$ Y ethanol	$\delta$ T/K	$\delta$ Y ethanol	$\delta$ T/K
0.20	0.093	0.806	0.066	0.550			0.081	1.873
0.40	0.063	0.125	0.044	2.250			0.016	0.368
0.60	0.078	0.000	0.012	1.650			0.016	0.163
0.80	0.004	1.600	0.000	0.150			0.028	0.236
0.90	0.016	0.082			0.013	0.141	0.004	0.125
0.95	0.023	0.125			0.011	0.094	0.006	0.236

It can be observed in Table 2 the low standard deviations of the experiments, expressed for the measurements of vapor composition and temperature.

### 3.2. Thermodynamic modeling results

Soares (2010) tested the Macedo et al. (1990) model in the prediction of the VLE of the system water-ethanol-potassium acetate at 0.06 mol.L<sup>-1</sup> and 766 mmHg. In the literature, Vercher et al. (1991) measured these data and the relative deviation of the model in comparison of the experimental data was 2.35% for temperature and 6.40% for ethanol vapor composition.

Because of the lowest deviation of the model tested by Soares (2010) and due to the fact that the sodium acetate had a similar behavior on the ethanol dehydration in comparison with

sodium chloride, calcium chloride and with the sodium acetate-potassium acetate mixture, new data were measured in the same concentration of potassium acetate to compare the experimental behavior and the model correlation.

Because of the same reason, the model was only tested for the solution with  $0.06 \text{ mol.L}^{-1}$ , to compare the results between sodium and potassium acetates. The model was not applied to the other solutions with different concentrations of salt because they showed to be supersaturated and this behavior is not desirable for the saline distillation.

Moreover, Figure 6 shows the experimental data measured in this work at  $0.06 \text{ mol.L}^{-1}$  compared to the predicted values from Macedo et al. (1990) model. All the predicted values are presented in Table 3 and Table 4 shows the relative deviations for temperature and ethanol vapor composition.

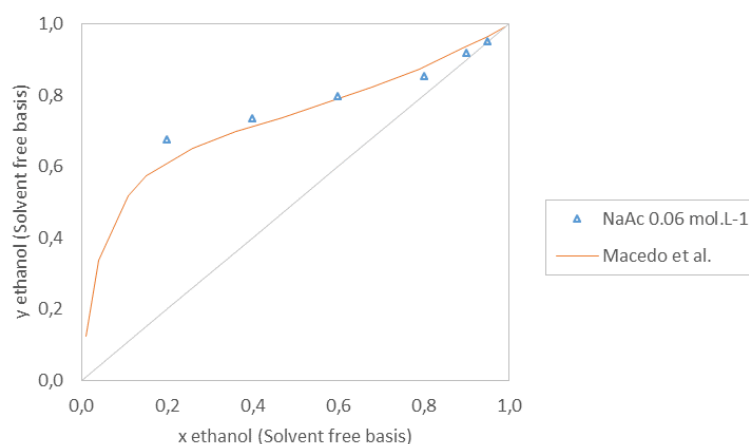


FIGURE 6 – Comparison between the experimental and predicted data for the VLE of water-ethanol-sodium acetate at  $0.06 \text{ mol.L}^{-1}$ .

TABLE 3 – VLE data of ethanol (1)-water (2)-sodium acetate (3) at 1 atm, calculated by the thermodynamic model

$x_1$	$x_2$	$y_1$	T (K)
0.01	0.99	0.122	373.85
0.04	0.96	0.337	367.05
0.11	0.89	0.517	360.25
0.15	0.85	0.575	357.95
0.26	0.74	0.652	355.15
0.36	0.64	0.698	353.85
0.47	0.57	0.738	353.15
0.57	0.43	0.778	352.75
0.68	0.32	0.823	352.45
0.79	0.21	0.874	352.25
0.89	0.11	0.932	352.15

0.95	0.05	0.965	352.05
0.99	0.01	0.993	352.15

\* Solvent free basis

TABLE 4. Relative deviations for temperature and vapor phase compositions between experimental and Macedo et al. (1990) model

$x_{\text{ethanol}}$	$y_{\text{ethanol}}$	T (K)	DR <sub>y</sub> (%)	DRT (%)
0.20	0.677	353.95	3.90	0.43
0.40	0.736	353.25	0.26	0.03
0.60	0.797	352.55	2.48	0.37
0.80	0.854	351.85	2.33	1.70
0.90	0.918	351.85	1.46	2.33
0.95	0.953	352.05	1.26	4.09

The model well correlated the experimental data with average relative deviations of 1.49% in temperature and 1.95% in vapor phase composition. All the experimental data for the system water-ethanol-sodium acetate, at different concentrations, are condensates in Figure 8, in function of temperature. There is also, in this figure, the VLE of ethanol-water system without any solvent to compare the influence of the salt. It can be seen that the salt was effective in the enrichment of ethanol in the vapor phase and the model corroborated this behavior.

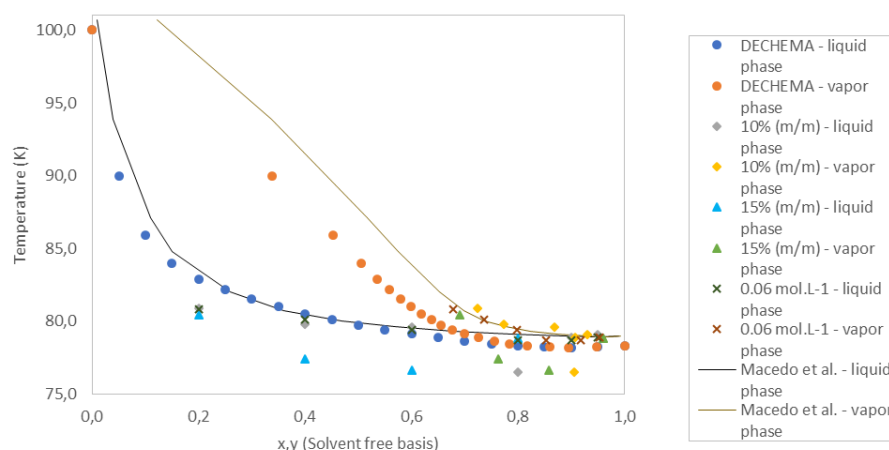


FIGURE 8. VLE data of the system water-ethanol-sodium acetate, at different concentrations, at normal pressure.



## 4. CONCLUSIONS

In this work, it was measured VLE data, at normal pressure, of the system ethanol-water-sodium acetate, at different concentrations, because there were not any data already published in the literature.

It was observed that, at low molar fractions of ethanol, the ethanol composition was enriched in the vapor phase and the system behaves satisfactorily. In contrast, at high concentration of the salt, sodium acetate did not well solubilize and the azeotrope was not broken and the results at higher concentration of ethanol in the solution were not satisfactorily. Moreover, the system with very low concentration of sodium acetate had the better results due to vapor phase enrichment in ethanol, even in the azeotrope concentration.

The experimental data were well correlated by the electrolyte model proposed by Macedo et al. (1990) with low relative deviations in temperature (1.49%) and vapor phase composition (1.95%).

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