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THE EFFECT OF KOH AND KCL ADDITION TO THE DESTILATION OF ETHANOL-WATER MIXTURE

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Abstract. This paper discuss the addition of KOH and KCl to the destilation of ethanol-water mixture. The investigation were on the azeotrope point in destilation curve, the yield of ethanol as the destilation product, and also on colligative and thermodynamic properties. Meanwhile, the thermodynamics parameters were the change on Gibbs energy of mixing, ΔGmix , the entropy of mixing, ΔSmix and the evaporation enthalpy of mixture, ΔHvap. The result shows that the addition of electrolyte KOH and KCl eliminated azeotropic point as it is described in T-x distillation curve. In addition, the ethanol yield increased, the Gibbs energy of mixing, DGmix, reduced, that indicates the mixing process occurred spontaneously. The spontaneity is also supported by the value of the entropy of mixing, DSmix, which is positive. It refers to the increasing of irregularity, confirming the spontaneity of mixing process. Meanwhile, the enthalpy of evaporation, DHvap, of ethanol-water mixture 300.1105 kJ/mol. The enthalpy increase to 738.4329 kJ/mol when KOH was added and the enthalpy value is 340.2338 kJ/mol when KCl was added. It indicates that water as main component in the mixture became more difficult to vaporize and it allowed the ethanol molecules to be freely released during destillation.

Keywords: azeotrope, colligative properties, distillation, addition of electrolyte, ethanol-water, thermodynamic properties

Introduction

Energy crisis led to rising fuel prices globally. It was challenged the word to explore alternative energy sources that are renewable and environmentally friendly, one of them is bioethanol. Generally, bioethanol is made from plants containing sugar derivatives such as sugar cane, sweet sorghum and beets and other starchy crops such as maize, cassava, yam and sago. Excess ethanol as an energy source is renewable energy, it can also reduce emissions as a result of carbon monoxide (Bailey, 1996).

High purity of ethanol is required for fueling objective. Meanwhile, the bioethanol processing into ethanol through fermentation and distillation only produce 35-40% of ethanol (Razmovski & Vučurović, 2012). It is known that the ethanol-water mixture provide an azeotrope point in destillation process under atmopheric pressure. The azeotrope point is when the composition of liquid and vapor similar and it become difficult to separate by the usual distillation. Therefore, other methods are needed to separate the azeotropic mixture of ethanol-water, one of them is the addition of electrolytes. The electrolytes must have special characteristics to achieve the desired separation as follows: their ability to break the azeotrope, ease of handling, low toxicity, simple recoverability and selective dissolution (Lladosa et al., 2007; Soares et al., 2015). NaOH is an electrolyte that is commonly used in the industry of ethanol production. However, actually NaOH addition on ethanol production may harm the environment. It because the sodium ions can replace calsium or magnesium ions (soil nutrients) in the soil, then damage the soil structure and pores, decrease cycle of water molecules and air, decrease the bioactivity and transfer of nutrients in the soil, and also increases the water release from soil. High concentration of sodium ions in soil also increase the pH of soil and poisons the plants (Halliwell et al., 2001; Laurenson et al., 2012). Therefore, it is necessary to study other substances to replace NaOH, that has similar function on destillation but provide no harmness to environment.

KOH and KCl provide similar properties with NaOH which are strong electrolyte, soluble in water in which the solubility of NaOH in water is 1110 g/L, the solubility of KOH in water is 1210 g / L and the solubility of KCl in water is 279 g/L. In addition, kalium ions in KOH and KCl are a kind of macro nutrient that is required for plant growth (Gunadi, 2009).

The addition of electrolytes might change the colligative properties of solution. Colligative properties are properties as the function of dispersed phase quantity. When the electrolyte is dissolved in a liquid, the saturated vapor pressure of the liquid will decrease and lead to increase the boiling point. Therefore, the boiling point of water in mixture is higher than pure water. However, the KOH and KCl molecules in the mixture will cause salting out of ethanol and increase the volatility of ethanol to become easily separate from the mixture (Lei et al., 2014).

A previous study on addition of NaOH and KOH has been conducted to separation of ethanol-water mixture by using a two-column fractional destillation (Stauffer, 2012). The research aimed to produces more ethanol volume toward volume ratio of ethanol-water mixture, as aimed by other research by adding KCl to ethanol-water mixture and produce 98%(v/v) of ethanol (Pinto wt al., 2000).

This research used a vigreux column instead of fractionation column as it was used by other researchers (Pinto et al., 2000; Stauffer, 2012). The effects of electrolyte addition were detected from the change of vapor-liquid equilibrium curve (Hadler et al., 2009), the yield of ethanol as distillate, and the change of thermodynamic parameters.

Experimental

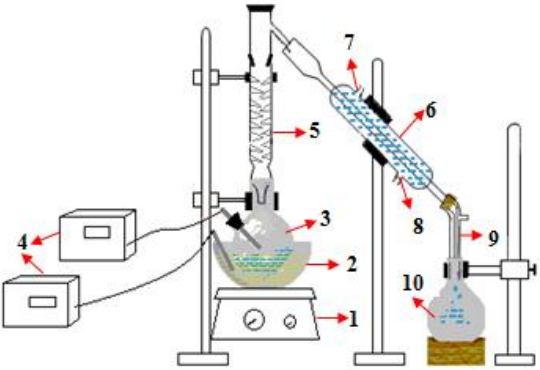
This research used ethanol for analysis (Merck) with purity of 99.9% which then was mixed with distilled water at various composition as depicted in Table 1. The electrolyte used were KOH at pro analysis grade (Riedel-de Haën), pro analysis grade KCl (Merck) and distilled water.

Table 1. Weight and volume composition of ethanol-water mixture

Ethanol		Water	
Weight (%)	Volume (mL)	Weight (%)	Volume (mL)
0	0	100	100
20	25	80	80
40	51	60	60
60	76	40	40
80	101	20	20
90	114	10	10
95	120	5	5
100	126	0	0

Destillation was conducted with vigreux column (Pyrex and Scott) equipped with a thermocontrol (a standardized home made), magnetic stirrer and boiling stone. The scheme of distillation flask is described in Fig. 1. In order to understand the effect of electrolyte, KOH or KCl was added at 1 mol in every kg of ethanol content in the mixture.

Boiling temperature or named as bubble point temperature was recorded when the ethanol-water mixture boiled. Meanwhile, the dew point temperature was recorded when the vapor reached saturation as it was shown by condensation inside the distillation flask. Distillation was stopped when the distillate stopped to drop. Then, the distillate was removed to be analyzed by gas chromatography (Buck Scientific Model 910, FID detector, 30 m Restek MXT-1 column). The experimental procedure, for all the electrolyte investigated, was done in triplicate. All experiments were performed under atmospheric pressure.



1. Hot Plate
2. Oil bath
3. Distillation flask
4. Thermo control
5. Vigreux column
6. Condenser
7. Water out
8. Water in
9. Adapter
10. Distillate flask

Fig. 1. Scheme of the experiment

The recorded boiling and dew points then were plotted on T-*x* vapor-liquid equilibrium curve to analyze the present of azeotrope point. The *x* is the mole fraction of ethanol in water and T is boiling and dew point temperature.

Meanwhile, the colligative properties was investigated through calculation of boiling point elevation, K_b, as depicted in Eq (1).

$$\Theta = m \,.\, K_b \tag{1}$$

m is the molality of solute (ethanol) and θ is the difference of the initial boiling point and the final boiling point. The main consideration of this model is based on the fact that all electrolytes are completely dissociated. In this model, when the electolyte was added, then the mixture become an electrolyte solution, therefore the boling point elevation, θ, beared the mean activity coefficient, $\gamma_{\pm}$, as depicted in Eq (2).

$$\theta = v\, K_b\, m \left(1 + \frac{1}{y\pm}\right) \tag{2}$$

with $m\ (1 + 1\ /\ \gamma_{\pm})$ is the molality of the solute after considering the coefficient activity of solution., *v* is the stoichimetric amount of positive and negative ions in the solution or mixture.

The Gibbs energy of mixing, ΔG_{mix}, was calculated using Eq (3), the entropy of mixing, ΔS_{mix}, was calculated by Eq (4), and the enthalpy of vapour, ΔH_{vap}, was calculated by Eq (5).

$$\Delta G_{mix} = RT(n_1 \ln x_1 + n_2 \ln x_2 + n_1 \ln \gamma_1 + n_2 \ln \gamma_2) \tag{3}$$

$$\Delta S_{mix} = -R(n_1 \ln x_1 + n_2 \ln x_2 + n_1 \ln \gamma_1 + n_2 \ln \gamma_2) \tag{4}$$

$$\ln a = \frac{\Delta H}{R}\left(\frac{1}{T}\right) + c \qquad (5)$$

Results and discussion

Vapor-liquid equilibrium of ethanol-water binary system

The T-x vapor-liquid equilibrium curve that was developed as variation of ethanol mole fraction whithout electrolyte addition, x, is described in Fig. 2(a). The vapor-liquid equilibrium curves of ethanol-water is compared to other result (Fig. 2(b)) in which the distillation was conducted without electrolyte addition (Carey & Lewis, 1932). The binary system of ethanol-water has azeotrope point at 89% mole fraction at 78.15°C(Carey & Lewis, 1932), The result of this experiment shows closed result at 88% mole fraction at 78.35°C. Typical of both curves are similar, in which at 0 % of ethanol mole fraction or it is known as pure water, the boiling point is at 100 °C, and more content of ethanol lead to decreasing of boiling point. The azeotrop point is at 78.35°C which is lower than the boiling point of pure ethanol (x= 100 % at 78.4 °C). At the azeotrope point, ethanol molecules could not separated from water molecules.

The vapor-liquid equilibrium curve of ethanol-water mixture after the addition on KOH and KCl are described in Fig. 3(a) and Fig. 3(b). It is evident that electrolyte modifies the vapor–liquid equilibrium curve, eliminating the azeotrope and allowing obtaining high purity ethanol. Gil et al. (2008), Lei et al. (2014), Lei et al. (2000), Pinto et al. (2000) and Soures et al. (2015) report that the electrolyte used as entrainer eliminate the ethanol–water azeotrope and change the VLE curve. Potassium cloride is well known as entrainer in extractive distillation of ethanol–water mixtures with a good performance results.

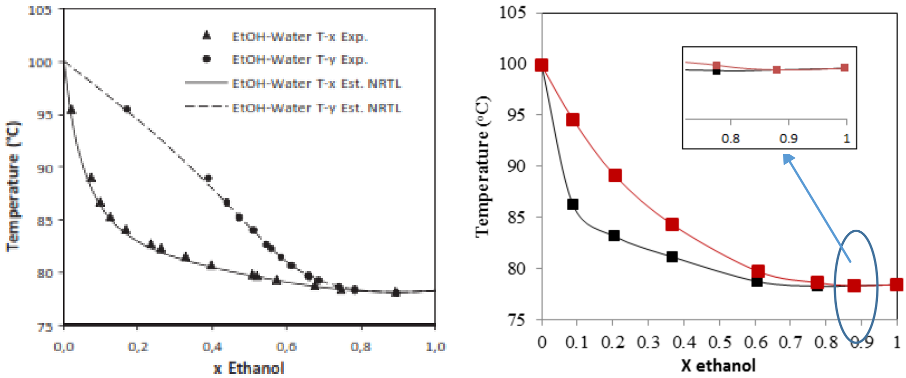


Fig. 2. Vapor-liquid equilibrium curve at 1 atm for ethanol-water mixture. (a) T-x curve; (▲) *T-x* Carey; (●) *T-y* Carey; (▬)*T-x* NRTL; (---) *T-y* NRTL(Carey & Lewis, 1932); (b) *T-x* curve of ethanol-water experiment; (🟥) Dew point; (■) Boiling point (experimental data)

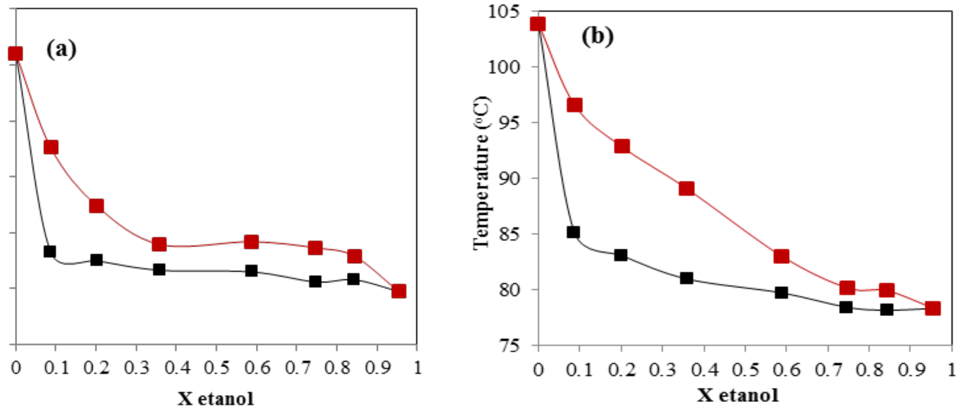


Fig. 3. Ethanol-water-electrolyte equilibrium curve at 1 atm (a) ethanol-water-KOH equilibrium, (b) ethanol-water-KCl

When ethanol molecules were easily removed from the mixture, then the distillate become richer with ethanol than the distillate before electrolyte addition on distillation process. It is supported by GC analysis on the produced distillate. The ethanol content in distillate before electrolyte addition for distillation process is 42.3 %. The ethanol content increase to 58.5 % after addition of KOH and it increase to 64.5 % after addition of KCl. In this studied conditions, the electrolyte that present the better effects is potassium chloride. This fact can be explained by the higher solubility of this electrolyte in water, producing a higher capability of interaction of the ions with the water, causing a higher salting-out effect (Soares et al., 2015).

Fig. 3. shows that the addition of KOH and KCl electrolyte increased the boiling and dew point. It is known that water molecules could interact with ethanol molecules through hydrogen bonding. When the electrolyte was dissolved into the mixture, the electrolyte molecules would dissociate into ions, in which those ions bear charge and having ability on providing coulombic interaction with water and ethanol molecules. The higher interaction of the electrolyte with the more polar component, altering, in this manner, the properties of the system ethanol-water mixtures (Soares et al., 2015). In addition, the water molecules would promptly surround the ions or it is called as hydration process. Therefore, those would reduce the possibility of water molecules to be oriented to ethanol molecules. The proposed mechanism is described in Fig. 4. When the interaction of ethanol-water becomes weak after electrolyte addition, the ethanol molecules will be easily separated from water and it allows elimination of azeotrope point.

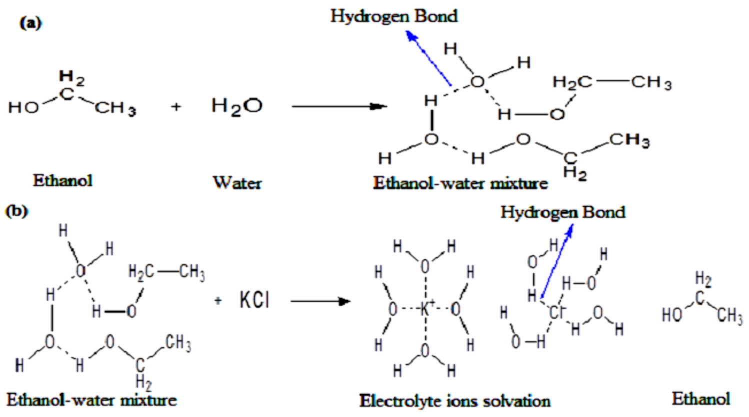


Fig. 4. The proposed mechanism of interaction between (a) ethanol-water mixture (b) ethanol-water-electrolyte mixture

Boiling point elevation constant (Kb) of ethanol-water and ethanol-water-electrolyte mixture

Plot of ethanol molality to the change of boiling point is described in Fig. 5(a). The plot shows that the curve follows exponential trend and does not follows the linear relation as it is stated by Eq (1). It indicates that the mixture does not comply to the ideal behaviour of solution due to the electrolyte content. The electrolyte which was dissociate into ions will change the ionic strength of the mixture system and lead to the mixture to deviate from its ideal behaviour. The plot also imply that the boiling point elevation has negative value, indicates that the boiling point was decreased instead of increased. It is caused by the higher volatility of ethanol than water. When the curve is isolated on three point with linear relation (Fig. 5(b)), it is found that the slope value is also negative.

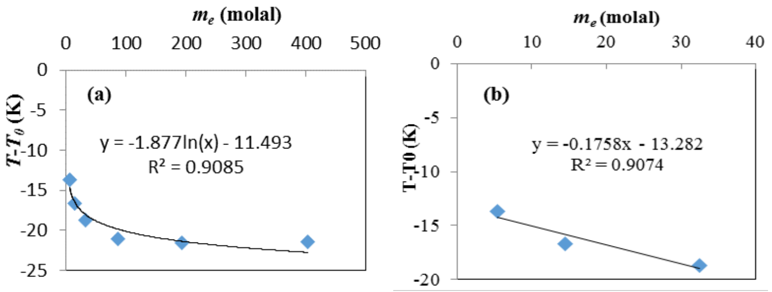


Fig. 5. Graph of solute (ethanol) molality versus boiling point elevation in ethanol-water mixture (a) in the 20-95% (w / w) ethanol (b) in 20-60% (w / w) ethanol, where T is the boiling point of the ethanol-water mixture, T_0 is the boiling point of water, m_e is the molality of solute (ethanol)

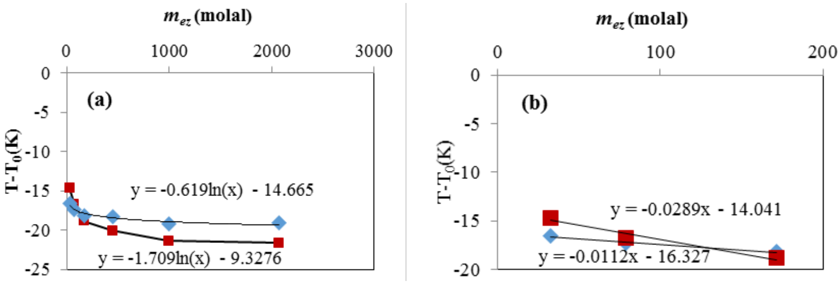


Fig. 6. Graph of solute (substance ethanol + electrolyte (KOH and KCl)) molality versus boiling point elevation of ethanol-water-electrolyte mixture (a) in 20-95% (w/w) ethanol (b) in 20-60 % (w/w) ethanol. (♦) ethanol-water-KOH mixture; (■) ethanol-water-KCl mixture, where m_{ez} is the molality of solute (ethanol-electrolyte)

When the graph of boiling elevation after the addition of KOH and after the addition of KCl are compared (Fig. 6(a)), it is known that the KCl addition allows lower boiling point than the addition of KOH. Linear plot on the straigh line of both curve imply that the KCl addition produced higher negative slope value than KOH addition.

Thermodynamics parameters

Mixing of ethanol-water and ethanol-water-electrolyte was performed at atmospheric pressure and 25^{O}C. The Gibbs energy and the entropy of mixing were determined using Eqs (3) and (4), where activity coefficient value (γ) of ethanol is assumed to be worth one, equivalent with γ of water, while coefficient activity of electrolyte from the calculation is 0.69.

Table 2. Gibbs energy of mixing (ΔG_{mix}) (J)

Ethanol (% w)	ΔGmix Ethanol-water (J)	ΔGmix Ethanol-water-electrolyte (KOH dan KCl) (J)
20	-3625,98	-4931,37
40	-5301,42	-6570,25
60	-5752,58	-6978,49
80	-4726,93	-5900,90
90	-3304,03	-4447,29
95	-2139,34	-3265,69

Table 3. Value of entropy of mixing (ΔS_{mix})

Ethanol (% w)	ΔSmix Ethanol-water (J/K)	ΔSmix Ethanol-water-electrolyte (KOH dan KCl) (J/K)
20	12.17	16.55
40	17.79	22.05
60	19.30	23.42
80	15.86	19.80
90	11.09	14.92
95	7.18	10.96

The Gibbs energy of mixing of ethanol-water at various composition of ethanol are negative (Table 2), indicating the spontenous process of mixing. The polarity of both ethanol and water allows them to mix sponteaneously. Meanwhile, after the addition of electrolyte, the Gibbs energy of mixing becomes more negative, implying spontaneity increasing. The presence of electrolyte in the mixture able to reduce the intermolecular interaction between water and ethanol, and the ions are in strong interaction with water, due to high solubility of ions in water than in ethanol The sponteous mixing process is supported by calculated the entropy of mixing, ΔS_{mix} as it is listed in Table 3.

High value of entropy indicates a disorder arragement of molecules in the mixture. When electrolyte was added, it will break the water-ethanol molecules interaction which arranged regulary, with weaken of water-ethanol interaction then re-arrange the bound between water-electrolyte-ethanol. In a binary system, the gibbs free energy change will has a reverse curve with the entropy, as it can be seen in Fig. 7 (a) and Fig. 7(b). The Fig. 7 shows that the gibbs free energy of mixing will reach the lowest value, in which the mixture form at highest spontaneity, and it will occurs when the mixture shows highest irregularity, confirming by highest entropi value.

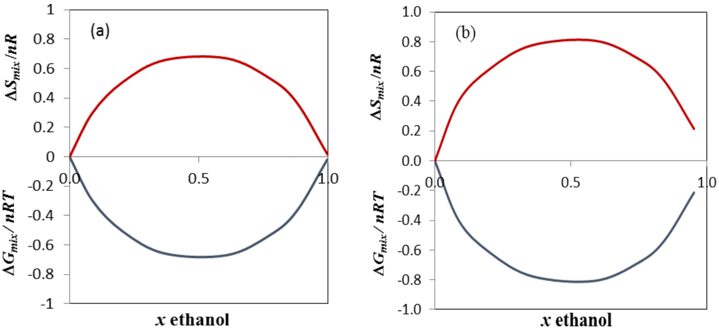


Fig. 7. The temperature variation of Gibbs energy and Entropy of mixing: (a) Ethanol-Water (b) Ethanol-Water- electrolyte (KOH and KCl); (▬) $\Delta G_{mix}/nRT$; (▬) $\Delta S_{mix}/nR$, where n is mols number, R is the general gas constant (8,314 J/mol K), T is room temperature (298 K), X ethanol is ethanol mol fraction

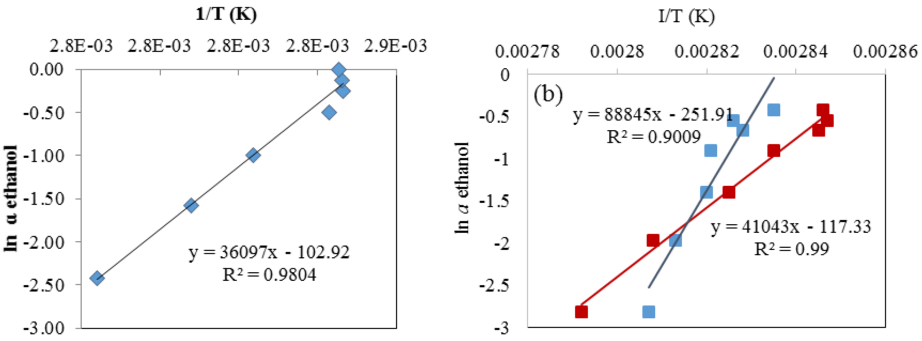


Fig. 8. The Plot of activity at various temperature (a). ethanol-water mixture, (b) ethanol-water-KOH (♦); ethanol-water-KCl. (■)

On the ethanol-water separation through destillation, a heat treatment is required to evaporate the mixture (ΔH_{vap} is endothermic). It means that the separation is an endothermic process. It is in agreement with the principle of chemical equilibrium, in which when the mixing of ethanol-water occur spontenously, therefore the reverse process to separate ethanol-water will occurs non-spontaneously. The lowest Gibbs energy and the highest entropy are occured at composition of 0.5 part of ethanol.

Enthalpy of vaporization was determined from a slope of plotting between ln *aa* versus 1/*T* (as it is stated by Eq (5)). In which *a* is activity of solution. The plot is described in Fig. 8.

The Activity plot (Fig. 8) shows the value of ΔH_{vap} from ethanol-water mixture is 300.11 kJ/mol. Meanwhile, after electrolyte addition the enthalpy of vaporization increase to 738.43 kJ.mol^{-1} and 340.23 kJ.mol^{-1} for KOH and KCl addition, respectively. The addition of KOH in ethanol-water separation has higher positive enthalpy value than KCl. This is due to KOH more soluble in water and ethanol than KCl, so that it required more energy to evaporate the mixture. It means that by add electrolyte, more energy will be required to vaporize the mixture. Therefore, when distillation was set up under boiling point of pure ethanol, the heat will only enough to vaporize ethanol and it become easily to separate from water with dissolved electrolyte.

Conclusions

Addition of electrolyte KOH and KCl to ethanol-water mixture could eliminate the azeotrope point and increase the ethanol content in the distillate by 42.3 % at initial to 58.5 % with KOH addition and 64.5 % with KCl addition.

The addition of electrolyte (KOH and KCl) in ethanol-water mixture caused the change of gibbs energy of mixing, ΔG_{mix}, to become more negative and the entropy of mixing, ΔS_{mix}, to become more positive. Both changes indicates that electrolyte addition lead to more spontaneous mixing. Meanwhile, electrolyte addition alows increasing of vaporization enthalpy, ΔH_{vap}, indicating more energy is required to vaporize the mixture. Therefore, when the distillation system was setup under boiling point of pure ethanol, the ethanol molecules will be easily vaporized without to be followed by water vapor.

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