

Effect of $MgCl_2$ and $CaCl_2$ on the bubble point of mixed solvent (Toluene-Isopropyl Alcohol- H_2O System)

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This study presents the effect of adding alkaline earth metal halides on the boiling points of mixed solvents (i.e., toluene-isopropyl alcohol-water system). The objective is to determine the effect of the salts on the selective separation of the solvents at azeotropic point. A comparison is made on two common Group IIA salts, $CaCl_2$ and $MgCl_2$. This comparison helps in setting the criteria for the economic viability of the technology and in setting options for the implementation of the technology. Though the research has been expanded to several types of solvent systems, this paper will present only the mixture of toluene, isopropyl alcohol and water.

Results showed that mixed solvents added with $CaCl_2$ boil at higher temperatures than those with $MgCl_2$ even though the latter salt is higher in molal concentration. This proves that $MgCl_2$, which is more electronegative than $CaCl_2$, is more effective in reducing the molecular affinity to polar and associating solvents (water and isopropyl alcohol) than to nonpolar solvent (toluene). The mixed solvent added with $MgCl_2$ registered higher boiling point deviation than those with $CaCl_2$, though both showed positive deviations. Either of the two can be effectively used and the data imply that shorter distillation tower can be used. Though the difference in temperature deviations of the two salts is statistically insignificant, a difference of one degree is economically significant considering the cost of energy.

Keywords: bubble point; azeotrope; salt effect; molecular affinity

INTRODUCTION

Organic solvents are commonly used in cleaning microchips, electronic devices and gadgets, machines and other process equipment or elements to remove dirt, grease, adhering mois-

ture, etc. Hence the industrial sector generates large amounts of spent solvents. These waste solvents contain as high as 90% of valuable organic solvents such as isopropyl alcohol, acetone, ethyl acetate, methyl ethyl ketone, ethanol and toluene.

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In the Philippines, industries are estimated to generate about 12,000 metric tons of spent solvents annually and this volume is steadily increasing. At this quantity, solvent recovery is a viable option. These organic solvents are hazardous and some are carcinogenic. Disposal and treatment of these types of wastes could pose major problems to the environment, health and safety. By recovering part or most of the valuable solvents, the amount to be disposed of or treated will be substantially reduced. As a result it will also reduce the hazards and potential environmental damage that the spent solvent pose. And for the industry, it will improve productivity through substantial reduction in operating cost and increased savings and income derived from the recovery of the solvents.

Separation of mixed solvents is traditionally done by distillation. However, there is a problem in recovering solvents at high purity due to the formation of azeotropes. Using typical distillation for these types of solvents require further purification.

This work has investigated the effects of the halide salts of calcium and magnesium on the bubble point temperature of a mixture of isopropyl alcohol, toluene, and water. This research is an expansion in terms of scope of the studies conducted earlier by the authors on the effect of alkali salt on the boiling point of a mixture of solvents [1, 2]. Examined are the bubble point variations in the presence of the salts that can lead to effective separation by averting azeotropic state. Also evaluated are the differences in the bubble points of the two salts and which salt gives a larger deviation from Raoult's law. A large deviation would mean a shorter distillation tower.

The bubble point comparison helps in setting the criteria for the economic viability of the technology and in setting the options for the implementation of the technology. Though the research has been expanded to several types of solvent systems, this paper will present only the mixture of toluene, isopropyl alcohol and water.

THEORY

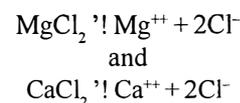
Current advances in molecular solution thermodynamics make it possible to separate selectively mixtures of compounds forming multiple azeotropes by conventional distillation [3]. One method is to reduce the molecular attractions among the species in solution by introducing a compound (or mass separating agent) that has greater molecular affinity to the species other than the one to be separated. The method has successfully worked for many binary systems [4].

In this study, the method is applied to a ternary system composed of toluene, isopropyl alcohol (IPA) and water. The technique involves the addition of an alkaline earth metal salt of one-cation-and-two-anions in a formula unit of the salt. The salt serves as the mass separating agent whose sole purpose is to alter the affinity of the systems water-IPA and IPA-toluene. At equilibrium, several intermolecular forces exist among the

five interacting species in solution. The species include the solvents, the cation and anions from the ionized salt and the unionized salt. The effect actually varies depending on the concentration of the salt. In this case, there are two anions for every cation generated. The molecular and ionic forces could result to the formation of different physical bonds such as dipole-dipole, hydrogen bonds, dimerization or even polymerization depending on the molecular structure (e.g., size and shape) of the species in solution and the type of ionic and molecular affinity among them.

This study examined the effect of the salts on the intermolecular forces or molecular affinities of the species in the mixture determined based on the deviation of the T-xy diagrams of the experimental results and the modified Raoult's Law. Tests for effectiveness of the separation were conducted using a fractionating column and analyzing the distillates collected by gas chromatography. This work has focused on the boiling point at azeotropic point of the solutions with and without salt and the degree of deviation in boiling point. Three concentration levels were evaluated for each salt: unsaturated, saturated and supersaturated at room temperature.

MgCl₂ and CaCl₂ are halide salts of Group IIA which are strong salts. These are the one-cation to two-anion type of salts. With complete ionization the total ion concentration is three times the molal concentration of the salt as shown below:



This suggests that a maximum rise in boiling point is expected to be three times the equivalent rise in BPR of a molal concentration of the salt. Hence the boiling point of the mixed solvents with MgCl₂ should be higher than those with CaCl₂. However, the results show otherwise.

Since the salts have high affinity towards water, they reduce its vapor pressure through the formation of physical ionic bonds (i.e., electrostatic effect). In limited amount, most of the salt will be attracted to the more polar substance. In this case, water is more polar than IPA. Toluene, which is non-polar, has no affinity towards the salt. Addition of the salt induces separation between the non-polar and polar solvents. Thus, the presence of the salt reduces the affinity of toluene for isopropyl alcohol. As the amount of salt is increased, the salt will reduce the vapor pressure not only of water but also isopropyl alcohol. IPA is slightly polar on the hydroxyl end. Thus, this will favor the release of more toluene into the vapor phase.

The overall effect of the molecular interaction explains the thermodynamic deviation of the mixture from ideal solutions. In theory, there are three possible significant molecular interactions that can be accounted for but these are often difficult or expensive to measure experimentally. They are usually deter-

mined using secondary data and extended UNIQUAC (Universal Quasi Chemical model) method or some other measurements such as osmotic property for solutions with ionic species for the chemical potential estimation of the electrolytes.

Molecular interactions account for the deviations of the thermodynamics properties of the system. The deviations are due to combinatorial (g^C) (i.e., due to collision between two or more molecules); residual (g^R) (i.e., due to size and shape of the molecules); and, electrostatic (g^E) (i.e., due to attraction and repulsion of charge particles) effects. There may be other factors responsible for the deviation in property of the solution but they are assumed to be insignificant compared to these three. Thus the extended UNIQUAC equation of the excess Gibbs property of the solution can be written as the sum of the three molecular interactions.

$$g = g^C + g^R + g^E$$

These molecular interactions affect the thermodynamic properties of the solution. This explains the deviation of the vapor-liquid equilibrium behavior from Raoult's Law. To account these interactions, a modified Raoult's law was developed where it assumes that the gas and liquid phases in equilibrium are real. The generalized Raoult's Law where the vapor and liquid form real fluids is presented in Equation 1:

$$\sum_1^k y_{ji} \hat{\phi}_{ji} P = \sum_1^k \sum_1^n x_{ji} \gamma_{ji} P_i^{sat} \quad (1)$$

For systems that will form two liquid phases in equilibrium the equation is presented in Equation 2.

$$\left(\sum_{i=1}^k x_i \gamma_i P_i^{sat} \right)_\alpha + \left(\sum_{i=1}^k x_i \gamma_i P_i^{sat} \right)_\beta = \sum_1^k y_i \Phi_i P \quad (2)$$

where $i, j = 1, 2, 3, \dots, k$ or n

The subscript i refer to the species in phase j . Equation 2 is for systems forming two liquid phases α and β that are completely immiscible with each other. When the sum of the pressures exerted by the two phases is equal to the atmospheric pressure the mixture boils. Hence, the boiling point of the mixture is lower than those of the two phases. This equation is applicable to all types of systems even in the presence of electrolytes. The value of γ is approximated using mean ionic activity coefficient (γ^\pm). It depends on the nature of the species, the type of molecular interaction and within molecule group contribution. The symbol ϕ is the fugacity coefficient. Parameters ϕ and γ can be calculated using UNIQUAC and NRTL for non-electrolytes and extended UNIQUAC method, van Laar and Wohl expansion for electrolytes [5-6].

At a certain IPA concentration, the system starts to form two phases. The upper phase is toluene with dissolved IPA while the lower phase is water with dissolved IPA. IPA is distributed between two immiscible fluids such that at equilibrium the following Nernst Distribution Equation holds

$$K = \frac{[IPA]_{toluene}}{[IPA]_{H_2O}} \quad (3)$$

where K is the Nernst distribution constant and the chemical potential of IPA in the two phases are equal. The presence of a strong salt, such as CaCl₂, changes the value of K at different temperatures, which in turn affect the boiling point profile of the mixture.

Upon addition of salt the chemical potential of the aqueous layer will increase hence, the equilibrium will shift towards the toluene layer. Meaning, part of IPA will transfer to the toluene layer. The amount of IPA that will transfer is dependent on the chemical potential at the new equilibrium. The new equilibrium would have layers with different IPA concentrations from the former. The shift is due to the strong molecular attraction of the salt to water and practically no attraction to toluene. Thus in the above ternary system part of IPA is expelled from the water layer and goes to the toluene layer resulting to an increased value of K (equation 3).

During a typical distillation the chemical potential at equilibrium of the three, or more, species changes as the most volatile component concentrates in the vapor phase while the least volatile one remains in the liquid phase. As separation progresses, a point is reached wherein the concentrations of the three species in the liquid and vapor phases in equilibrium are equal. At this state (azeotropic point) the solution can no longer be separated due to the formation of a relatively stable intermolecular interaction. If the azeotropic condition is broken or averted, then separation of the components in equilibrium is possible. This research has developed a technique that averts the formation of an azeotropic condition during traditional distillation.

METHODOLOGY

The study was divided into two phases. The first was developing the design of the experiment. The full block model was designed with three levels based on solubility of the salts at room temperature [6]. The salt levels were 10 g/L, saturated and 85 g/L. The parameters tested were: (1) the effect of the amount salt on the boiling point; (2) phases at different mole fraction of the solvents in the solution; and, (3) comparison of the effects of CaCl₂ and MgCl₂ on the boiling points of mixed solvents. The amount of water was fixed while those of toluene and isopropyl alcohol were varied.

The second was the experimental part, which was further divided into two: one was the boiling point determination of different mixtures of IPA-toluene-water in the presence of $MgCl_2$ and the other in the presence of $CaCl_2$.

Mixtures of IPA-toluene-water were prepared in different volume ratios. Each mixture was then divided into four portions. Different amounts of the salt were added to three of these solutions. The first simulated the unsaturated solution of salt; the second corresponded to the saturated solution at near boiling; while the third simulated the supersaturated solution at the boiling point. These variations were used to determine how the boiling point behaved under multiple phase condition. The fourth fraction, which was left salt-free, served as the control. The solutions were then refluxed to observe the bubble points.

RESULTS AND DISCUSSION

The boiling point profiles of the system at different compositions without the salts are presented in Fig. 1. It can be observed that at a certain composition range two phases exist. This shows that at these compositions neither of the two organic solvents could serve as solvent for the other based on their mutual solubility with each other.

The two phases occur at about 18% to 60% IPA forming an envelope. These phases arise when toluene and water are both saturated with IPA. The upper layer is toluene-IPA system while the lower is water-IPA. Similar but more pronounced separation is observed when salts are added. Apparently the salt that dissolves in water but not in organic layer releases part of IPA to the toluene layer.

Figure 2 presents a boiling point profile that shows the effect of the concentration of the salt on the boiling point of the system. It illustrates that the addition of salts allows more toluene to escape into the vapor phase (i.e., by decreasing the vapor pressure of both water and IPA). When a small amount of salt is added (0.11 molal) the decrease is lesser. The results show that mixed solvents with $CaCl_2$ boil at higher tempera-

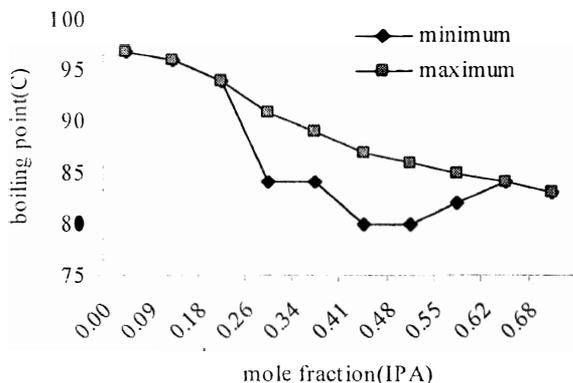


Fig. 1. Boiling point profile of IPA-toluene-water mixtures.

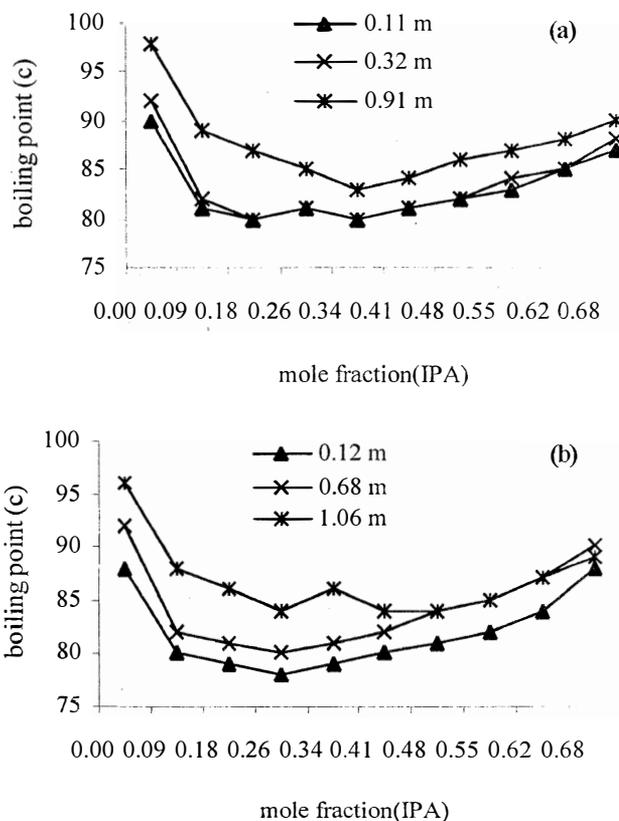


Fig. 2. The boiling point profiles of mixed solvents with (a) $CaCl_2$ and (b) $MgCl_2$ at different salt concentrations.

tures than those with $MgCl_2$ even though the latter salt is higher in terms of molal concentration. The solvent mixture with $MgCl_2$ is showing the effect of molecular affinity while the mixture with $CaCl_2$ is starting to manifest the colligative effect [9]. This proves that $MgCl_2$, which is more electronegative than $CaCl_2$ is more effective in reducing the molecular affinity to polar and associating solvents (water and isopropyl alcohol) than to non-polar solvent (toluene).

Figure 3 shows a comparison of the boiling point profiles of the two salts. At the lower concentration range where their relative molal concentrations are almost equal (0.12 m $MgCl_2$ and 0.11 m $CaCl_2$), the mixed solvent with $MgCl_2$ registers lower boiling point in most cases although more $MgCl_2$ is present. This is even more apparent when 80 g/L salt is added. This amount is equivalent to 1.06 m $MgCl_2$ and 0.91 m $CaCl_2$. Both salts have van't Hoff factors equal to three. Though, statistically this is not significantly different, a small difference in temperature may mean a substantial energy saving.

A statistical comparison is made on the effect of increasing the amount of salt. It is evident that increasing the amount of salt increases the boiling point. Theoretically, one would expect that as more salt is added more water and IPA will be held back

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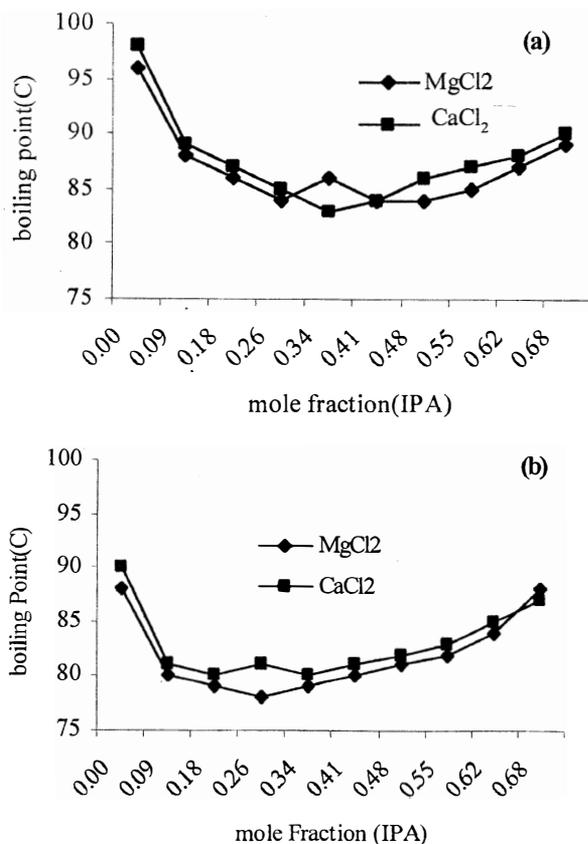


Fig. 3. The graph on top (a) shows the boiling point profile of mixed solvents with of 1.06 m $MgCl_2$ and 0.91 m $CaCl_2$. The graph below (b) is the plot of 0.12 m $MgCl_2$ and 0.11 m $CaCl_2$.

in the water layer. If this were the case then the boiling point should go down further. However, with more salt added the colligative effect starts to dominate [9]. Beyond 0.32 molal, the boiling point rose sharply indicating that the colligative effect became dominant to both salts.

Compared to ideal solutions (i.e., solutions behaving according to Raoult's Law) the mixed solvents added with $MgCl_2$ register higher boiling point deviation than those with $CaCl_2$ [5]. The deviation is more pronounced at the supersaturated level but this is not statistically significant when the two results are compared numerically. However, a single temperature unit deviation could mean a substantial saving in energy cost. The observation also implies that a shorter distillation tower can be used to effectively separate the solvents; hence, lower capital investment costs.

This finding is economically interesting because $MgCl_2$ is relatively cheap and can be easily regenerated for reuse. Also, the mixed solvents can be distilled at lower temperature implying lower energy costs. This technological option can greatly benefit the semiconductor and all other industries generating spent solvents. The benefits include decreased volume of spent solvents to be stockpiled, savings from the cost of waste handling and income derived from the recovered solvents.

CONCLUSION

In conclusion, $MgCl_2$ is a better salt than $CaCl_2$ in modifying the molecular affinity between IPA and toluene system and in reducing the vapor pressure of water and IPA. It can also lower the boiling point of the solvent system to a farther extent than $CaCl_2$.

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