

Interpretation And Co-Relation of Vapour Liquid Equilibrium Data In Distillation By Using Salt Effect For Propanol-Water System

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Abstract- Vapour-liquid equilibrium (VLE), is a condition where a liquid and its vapour (gas phase) are in equilibrium with each other or more precisely a state where the rate of evaporation equals the rate of condensation on a molecular level such that there is no overall vapor-liquid inter conversion. In this paper we study the azeotrope breaking of binary 1propanol-water system with salt-added method to recover purity of water by using batch distillation and to investigate the concentration of salt added to break the azeotrope of 1propanol- water system in batch distillation process.

The objective of this paper was to study physical properties with different measurement methods and to supply thermodynamic data for several chemical systems.

Keywords- Distillation, 1Propanol, Binary system, thermodynamic modeling.

I. INTRODUCTION

In order to achieve the objective, some boundary or scope need to be specified. This project covers the breaking of azeotrope of binary 1propanol-water system, salt added method, batch distillation and Aspen Plus. The salt used is Sodium chloride, Calcium chloride, ammonium chloride. It is chosen for its highly availability and also it is the most common salt used in the industries. The concentration of salt use in this project will vary to get the optimum concentration. Secondly is to run several simulations using Aspen Plus to get optimum results. So, certain parameters will take place in order to achieve the objective. The parameters consist of Concentration of salt added, density and temperature.

Due to this difficulty the solids salts are considered better than the liquid separating agents as they produce a solvent-free extract and requires no other separating column. The salt dissolved in a mixed solvent may affect the boiling point, the mutual solubility's of the two liquid components, and the equilibrium vapour phase composition. Generally, the

ions of the dissolved salt tend to attract, the molecules of the more polar component by the electrostatic field of the ions and thereby enriching the vapour composition of the less polar solvent, in which the salt isles soluble.

The measured systems were chosen not only for their industrial importance, but also for the scarcity of data available in the open literature. In fact, thermodynamic data are fundamental for modeling process units, and in particular separation units. An accurate representation of the phase separation may be sufficient to design full scale separation plants, such as distillation columns. This was successfully achieved in this work through targeted experimental investigations and thermodynamic modeling of chosen systems. A good understanding of VLE is indispensable in the design and control of distillation systems.

II. LITERATURE REVIEW

Favzibanat Sameer al aseh et al., analysed that The VLE of the propionic acid-water system under no salt condition and in the presence of four chloride salts (NaCl, NH₄Cl, CaCl₂, AlCl₃) dissolved to various concentrations were studied at 40 and 50.8°C. The chloride salts used in this work have a salting-out effect on propionic acid in the following order: AlCl₃ > CaCl₂ > NaCl > NH₄Cl. The enhancement factor was mainly dependent on the salt type and concentration, rather than on temperature. Increasing salt concentration led to the increase of salting out of propionic acid.

A.T.Tok et al., studied that the vapour liquid equilibrium of water-ethanol-2-propanol was experimentally found to be affected by the addition of NaNO₃, NaCl, KCl or CH₃COOK. All these salts salted-in water more than ethanol and 2-propanol and all except NaCl salted-in ethanol relatively more than 2-propanol. These effects were well predicted by Tan-Wilson and Tan-NRTL models.

Shuzo Ohe et al., analysed that If the salt is more soluble in a less volatile component, then the relative volatility will be raised, because of the lowered vapour pressure of the less volatile component. The salts are more soluble in methanol, the less volatile and thus increasing relative volatility. On the other hand, the salt effect increases within creasing solubility ratio of salt in acetone to methanol at the concentration from 60 to 100mole %acetone.

Emestoverchr et al., The addition of lithium nitrate to acetone+methanol system produces an important salting out effect on the acetone, and the azeotrope disappears at salt mole fractions higher than 0.022. This effect is stronger than that produced by sodium iodide, sodium thiocyanate, and calcium bromide on this system.

Maria C, Iliuta et al., examined that in the acetone-methanol- NaSCN system, across over effect between salting-in and salting-out on acetone was observed as in the case of NaI, the transition from salting-in to salting-out takes place at an acetone mole fraction (saltfree basis) of about 0.3 for the NaSCN and 0.2 for the NaI system. In the case of NaSCN, the azeotropic point can be eliminated ata salt mole fraction higher than 0.03. A stronger salting-out effect and a weaker salting-in effect on acetone was observed in NaI compared to NaSCN. crossing point between the dew point and the bubble point curves was also found for the acetone -methanol-NaSCN system, in case NaI.

S abderafi et al analysed that attention is given to adapting the PR EOS for industrial sugar juices using the pseudo component approach. Industrial sugar juices were considered as aqueous solutions of sugar, amino acid, carboxylic acid and ash. The pseudo components composition can be obtained by analytical techniques frequently used in sugar industry. In future papers, the PR EOS will be used to predict other physical properties of industrial sugar juices and to simulate evaporation process of a sugar factory.

A.S. Narayana et al.,analysed that Addition of KCl, Na₂SO₄, and K₂SO₄ results in “salting out” of acetic acid. Water-acetic acid solutions containing salts KCl and Na₂SO₄above 80 and 91wt % water on salt-free basis, respectively, formazeotrope. An equation of the type $\log(Y_s/Y_0) = KW$ fits the data for the three salts studied in this system. All the three salts studied are found to have salting out effect for acetic acid in varying degrees.

III. EXPERIMENTAL SET UP

Experimental Determination of vapour-liquid Equilibrium Various methods for direct determination of equilibrium data are as follows:

1. Distillation method
2. Circulation method
3. Static method
4. Bubble and Dew point method
5. Flow method

The present experimental setup is based on the circulation method, so the basic theme of the setup and procedure the method is as follows.

CIRCULATION METHOD:

This method is the most commonly used, can easily be used both in the region of medium and low pressure. Various equilibrium stills with simple circulation differ significantly in their construction details but they all are based on a common principle.

Principle: As the vapors come out from the distillation flask „A“ they pass through the vapour conduit and after complete condensation collect in the receiver „B“. The liquid flows backward once the receiver is filled; a trap is generally inserted there to prevent the flow of liquid from the distillation flask to the receiver. If the still is started with the receiver B empty, at the instant at which it fills, its contents are richer in more volatile component than that of the vapour phase over the boiling mixture in the distillation flask. Operating further, the contents of the distillation flask become richer with more volatile component and the receiver becomes poorer. This process continues till the steady state is obtained, in which the compositions in both vessels no longer changes with time. Both compositions are determined automatically.

According to the manner of circulation of the phases, these stills are classified into two groups.

1. Still with circulation of the vapour phase.
2. Still with circulation of the vapour and liquid phase

These stills with minor modifications have been used in the present experimental work.

Apparatus and procedure:



Fig. 3.1 Experimental Setup

The still which was used in the present work had been designed to avoid and reduce faults and errors. The still was thoroughly washed with water and then with acetone. It was mounted over the hot plate magnetic stirrer. A condenser was mounted over the condensate chamber. A magnetic stirrer was used for stirring thereby maintaining homogeneity of the liquid to improve salt dissolution.

The main characteristic of the present design is that, the pot volume is much higher than the liquid condensate volume and at steady state only a few drops of condensate were collected and analyzed for the determination of the vapour composition. Due to which the composition of the liquid prior to the addition of the salt could well be taken as the equilibrium liquid composition without introducing appreciable error. The still was charged with 200 ml of 1-Propanol and water mixture of desired composition.

So, let us suppose

Volume of 1-propanol = v ml

So volume of water = $(200-v)$ ml

If n is the mole fraction of 1-propanol, then Analysis of Samples

The samples were analyzed by a method similar to the West phal Balance density determination technique. A “bob” was suspended in the condensed vapour sample and weighed to five significant figures with a Mettler H5 1 AR balance, which approximated the West phal procedure. The composition was calculated from a calibration curve derived

from measurements on standard solutions. The liquid composition was determined by material balance.

The salt additions and rinse aliquots were recorded in order to keep an accurate account of the liquid composition during the experiments. Later, after the condensate samples were weighed and their compositions determined the liquid compositions were further corrected for the amount and composition of the condensate in the condensate holdup chamber and the condensate samples themselves. The mass of the vapour in the vapour space of the still was not accounted for, nor was there any attempt to account for vapors escaping through the condenser or through the loading port during the salt additions at 20-30°C below the boiling point of the solution. This analysis does not take into account errors.

Reagents and Their Physical Properties:

A non-aqueous azeotropic system 1-propanol-water is selected for studying the salt effect. The system is found to form the minimum boiling azeotrope at 0.44 mole fraction of 1-propanol at a temperature of 87.70°C and local atmospheric pressure of 700 mm Hg. The used chemicals are supplied by S D Finechem Ltd, Mumbai, and are of analytical reagents grade. The physical properties of chemicals used are compared with the literature values and given in the following table. The solid salts are supplied by Fisher Scientific Ltd and of analytical reagent grade. All solid salts used are completely dried in hot air oven prior to use until the constant weight is not obtained.

Table 3.1 Physical properties of chemicals used

Component	Boiling Point	Boiling Point	Specific gravity	Specific gravity
	Reference	Present Study	Reference	Present Study
1-propanol	97.2	97.18	0.7997	0.7976
Water	100	100	0.9970	1.0000

Co-relation of VLE Data:

Data experimentally obtained should be co-related by proper co-relation equation to analyse the experimental work. The importance of correlating equations for vapour-liquid equilibrium data are to

- Correct scattered data
- Calculate vapour-liquid equilibrium data over the entire composition range.
- Calculate x - y curves at one temperature from those at another equilibrium data for

multicomponent systems which are difficult to obtain experimentally.

iv)Facilitate the prediction of the data in an abridged form convenient for compute calculations. Central to the correlation of VLE data are the thermodynamic excess properties, which describe the behavior of the liquid phase. These properties express the differences between actual property values of a solution and the values which would be exhibited by an ideal solution at the same temperature, pressure, and composition. The fundamental equation relating the compositions of the vapour and liquid under equilibrium is given by

$$y_i P = \gamma_i x_i P_i^O$$

Where,

y_i is mole fraction of component i in the vapour,

x_i is mole fraction of component i in the liquid,

γ_i is the activity coefficient,

P_i^O is saturation pressure of the liquid for the component i ,

P is the total pressure.

The activity coefficients γ_i vary with composition and temperature at a given pressure. In order to calculate the relationship between pressure, temperature and composition of the equilibrium phases for non-ideal solutions at low pressures where the vapour phase is assumed to behave as an ideal gas, provided that the equations relating the activity coefficients to compositions and temperature are available. Experimental vapour-liquid equilibrium data can be correlated using such equations and the empirical parameters in them are evaluated. Once an activity coefficient equation suitable for the given system is identified and the parameters evaluated, it can be used for vapour-liquid equilibrium calculations through. There are two methods by which the VLE data can be correlated. First, based on the equations for Gibbs free energy and second based on the local composition.

Using Slopes of $\ln \gamma$ Curves

The Gibbs – Duhem in terms of activity coefficient provides a very simple test for thermodynamics consistency.

$$x_1 (\delta \ln \gamma_1 / \delta x_1) = x_2 (\delta \ln \gamma_2 / \delta x_2)$$

This can be put into the following form

$$x_1 (\delta \ln \gamma_1 / \delta x_1) = - (1 - x_1) (\delta \ln \gamma_2 / \delta x_1) \quad (4.11)$$

Plot the logarithm of the activity coefficients against mole fraction x_1 of the component 1 in a binary solution as shown in fig. and measure the slopes of the tangents drawn to the resulting Curve sat any selected composition x_1 .

IV. RESULT AND DISCUSSION

System: 1propanol-water with 0.5 % NH₄Cl salt:

we selected ammonium chloride salt for shifting the azeotrope of 1propanol water system. It is insoluble in 1propanol but soluble in water up to 3to4%. The experimental vapour liquid equilibrium data for the system 1propanol-water in presence of 0.5% ammonium chloride salt is obtained..]The vapour pressure of each component at corresponding equilibrium temperature is calculated by using Antoine equation according to this vapour pressure activity coefficient data is tabulated. The plot of $\ln \gamma_1$ and $\ln \gamma_2$ vs. mole fraction is shown in figure(4.1).According to all below observation it is observed that azeotrope is shifted from 0.44 to 0.46 mole fraction of 1propanol due to addition of 0.5% ammonium chloride salt.

Table 4.1 Vapour Pressure and Activity Coefficient Data for 1propanol-water with 0.5% NH₄Cl salt

Vapour pressure for 1 propanol(p0) mmHg	Vapour pressure for Water (p0) mmHg	Activity Coefficient For 1Propanol (γ_1)	Activity Coefficient For Water (γ_2)	$\ln(\gamma_1/\gamma_2)$
806.425	741.21	0	0.9578	0
660.370	615.14	15.052	0.847	2.8764
522.0433	494.056	9.819	0.966	2.3183
507.144	480.899	3.677	1.052	1.2509
513.485	486.500	2.696	1.112	0.8849
484.459	460.8192	1.954	1.320	0.3917
494.682	469.857	1.535	1.440	0.0639
492.607	468.038	1.340	1.623	-0.1913
541.442	511.414	1.059	2.008	-0.6393
592.559	556.009	1.078	1.787	-0.5055
746.2103	689.427	0.951	0	0

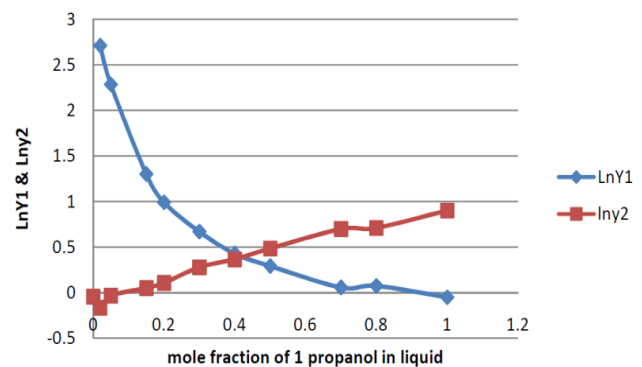


Fig.4.1 $\ln \gamma_1, \ln \gamma_2$ Vs mole fraction of 1 propanol in liquid with 0.5% NH₄Cl salt

The co-relation is checked by using three equations namely Margules, Van Larr and Chao’s modification of Redlich Kister equations. The constants for Margules equation, Van Larr equation and Chao’s modification of Redlichkister equation are tabulated. Table (4.1) shows the comparison of γ_1 calculated and experimental values. γ_1 calculated by Chao’s modification of Redlichkister equation are more close to that of experimental values. Thus, Chao’s modification of Redlichkister equation is more suitable for this

system than other equation. In other words. Chao’s modification of Redlichkister equation fits the experimental data well as compare to other equations. After addition of 0.5 % ammonium chloride salt solution become saturated that’s why by adding more salt we can’t shift the azeotrope.

System: 1propanol-water with 0.5 % NaCl salt

The experimental vapour liquid equilibrium data for the system 1propanol-water in presence of 0.5% Sodium chloride salt is obtained. The vapour pressure of each component at corresponding equilibrium temperature is calculated by using Antonie equation. The activity coefficient data are calculated..The plot of $\ln \gamma_1$ and $\ln \gamma_2$ vs. mole fraction is shown in figure(4.2).According to all above observation it is observed that azeotrope is shifted from 0.44 to 0.51 molefraction of 1propanol due to addition of 0.5% sodium chloride salt.

Table 4.2 Vapour Pressure and Activity Coefficient Data for 1 propanol-water with 0.5%NaCl salt.

Vapour pressure for 1propanol(p0) mmHg	Vapour pressure for Water (p0) mmHg	Activity Coefficient For 1Propanol (γ_1)	Activity Coefficient For Water (γ_2)	$\ln(\gamma_1/\gamma_2)$
800.386	736.037	0.000	0.964	0.000
655.239	610.660	22.755	0.927	3.199
515.703	488.380	33.042	0.944	3.554
498.884	473.510	9.798	0.926	2.359
510.387	482.760	6.120	0.915	1.900
476.430	453.690	4.231	1.008	1.434
490.568	466.221	3.401	1.008	1.215
590.568	464.413	1.418	1.560	-0.094
537.402	507.513	1.095	2.156	-0.677
590.201	553.913	1.054	1.956	-0.618
743.361	686.924	0.955	0.000	0.000

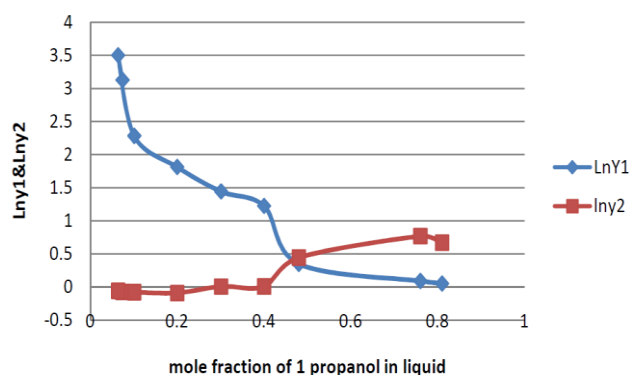


Fig.4.2 $\ln \gamma_1, \ln \gamma_2$ Vs mole fraction of 1 propanol in liquid with 0.5%NaCl salt

The co-relation is checked by using three equations namely Margules, Van Larr and Chao’s modification of Redlich Kister equations. The constants for Margules equation, Van Larr equation and Chao’s modification of Redlichkister equation are tabulated.

System: - System 1propanol-water with 0.5 %CaCl2salt

The experimental vapour liquid equilibrium data for the system 1propanol-water in presence of 0.5% Calcium chloride salt is obtained. The vapour pressure of each component at corresponding equilibrium temperature is calculated by using Antonie equation. The plot of $\ln \gamma_1$ and $\ln \gamma_2$ vs. mole fraction of 1propanol is shown in fig (4.3).According to all above observation it is observed that azeotrope is shifted from 0.44 to 0.45 mole fraction of 1propanol due to addition of 0.5% calcium chloride salt.

Table 4.3: Vapour Pressure and Activity Coefficient Data for 1propanol-water with 0.5%CaCl2salt

Vapour pressure for 1propanol(p0) mmHg	Vapour pressure for Water (p0) mmHg	Activity Coefficient For 1Propanol (γ_1)	Activity Coefficient For Water (γ_2)	$\ln(\gamma_1/\gamma_2)$
803.156	738.414	0.000	-	-
657.657	612.773	11.91	0.786	2.7172
519.876	492.152	8.322	0.940	2.1806
502.921	477.089	5.898	0.956	1.8188
515.584	488.314	2.967	1.034	1.0542
482.391	458.986	2.171	1.230	0.5678
494.652	469.785	1.614	1.385	0.1532
492.606	467.95	1.384	1.572	-0.1276
541.626	511.328	1.086	2.140	-0.6780
592.515	555.904	1.050	1.949	-0.6884
746.105	689.286	0.951	0.00	-

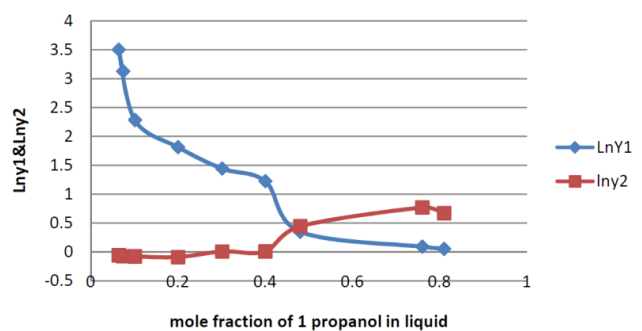


Fig.4.3 $\ln \gamma_1, \ln \gamma_2$ Vs mole fraction of 1 propanol in liquid with 0.5%CaCl2 salt

The co-relation is checked by using three equations namely Margules, Van Larr and Chao’s modification of Redlichkister equations. The constants for Margules equation, Van Larr equation and Chao’s modification of Redlichkister equation are tabulated.

V. CONCLUSION

The objective of this paper was to study physical properties with different measurement methods and to supply thermodynamic data for several chemical systems. The measured systems were chosen not only for their industrial importance, but also for the scarcity of data available in the open literature.

The VLE diagrams for all the systems mentioned previously are shown in Figures. Thus, it is concluded from

that the view point of separation of the binary mixture 1 propanol-water to its components by distillation, NaCl is more effective than other salt.

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