SALT EFFECT ON LIQUID LIQUID EQUILIBRIUM OF THE SYSTEM WATER + 1-BUTANOL + ACETONE AT 298K: EXPERIMENTAL DETERMINATION

A Thesis Submitted

By

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CERTIFICATE

This is to certify that the thesis entitled, **"Salt effect on LLE of the system water + 1-butanol + acetone at 298k: experimental determination**" submitted by **Sitansu Palei** for the requirements for the award of Bachelor of Technology in Chemical Engineering at National Institute of Technology Rourkela, is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the seminar report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Dr. P RATH
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Sitansu Palei **Date:**

ABSTRACT

The influence of a solid salt on VLE and LLE cannot be ignored because it significantly changes the equilibrium composition. Liquid-Liquid Equilibrium is the result of intermolecular forces which can significantly change due to salt addition which introduces ionic forces , affecting the thermodynamic equilibrium . Aqueous electrolyte liquid-liquid equilibrium is often related to extraction processes. In the present work the salt effect on the system namely '1-Butanol+Water+Acetone' has been studied with various salts under varied concentration at 298K. The salt used in the above system are NaCl,KCl with 5%,10% and 15% concentration. The solubility data and tie-line data are taken experimentally at different salt concentration. The experimentally determined tie-line data of this work have been correlated by Hand's correlation.

KEYWORDS: Liquid–liquid equilibrium; Data; Salt effect; Experimental; Correlation

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LIST OF SYMBOLS

A	Water
B	1 – Butanol
C	Acetone
X_A	Mass fraction of Water
X_B	Mass fraction of 1-Butanol
X_C	Mass fraction of Acetone
X_{AA}	Mass fraction of Water in Water layer
X_{AB}	Mass fraction of Water in Butanol layer
X_{BA}	Mass fraction of 1-Butanol in Water
X_{BB}	Mass fraction of 1-Butanol in 1-Butanol layer
X_{CA}	Mass fraction of Acetone in Water
X_{CB}	Mass fraction of Acetone in Butanol layer
X_S	Salt Percentage
a,b,c,d	Constants for Eisen-Joffe and Modified Campbell Equation.
Ln A, B	Constants for Hand’s Plot

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CHAPTER-1

1.1 INTRODUCTION

Aqueous solutions containing salts are of increasing importance and influence on separation processes in chemical engineering. The electrolyte influence must be considered both in process design and operation, because it can significantly change the equilibrium composition. Aqueous liquid–liquid equilibrium is the results of intermolecular forces, mainly of the hydrogen–bonding type; addition of a salt to such systems introduces ionic forces that affect the thermodynamic equilibrium. When the mutual solubility decreases due the salt addition, the size of the two–phase region increases, and this effect is called “salting-out”. In the opposite, when the solubility increases, the effect is called “salting-in”. The salting–in effect can be used to remove organic compounds from water. [6]

Aqueous electrolyte liquid–liquid equilibrium is often related to extraction processes. For instance, the ethyl acetate recovery from its mixture with ethanol involves an aqueous extraction step in order to remove the ethanol. In this case, it is important to decrease the mutual solubility’s of water and ester, improving the separation and yielding a dryer ester. [6]

The separation by solvent extraction becomes increasingly more difficult as the tie-line becomes parallel to the solvent axis, as shown in solutropic solutions. By adding an adequate salt, the mutual solubility of the mixture can be significantly changed, in order to modify the slope of the tie-lines, even to the extent of eliminating the solutrope. [6]

The presence of an electrolyte in a solvent mixture can significantly change its equilibrium composition. The concentration of a solvent component in a liquid phase of liquid-liquid system increases if component is salted in and decreases if it is salted out of the liquid phase. This salt effect has been advantageously used in solvent extraction. Separation by solvent extraction becomes increasingly more difficult as the tie-lines become parallel to the solvent axis as in the case of solutropic solution. By adding a suitable salt the tie-line of a LLE mixture can be significantly changed, even to extent of eliminating the solutrope.

1.2 IMPORTANCE AND APPLICATION

The addition of an electrolyte to solvent mixtures changes the interaction among the various solvent and solute molecules resulting in shifting their phase equilibrium even to the extent of eliminating solutrope in liquid equilibrium. In an aqueous-organic solvent mixture, addition of an electrolyte generally salts out the organic solvent molecules thus enriching the organic phase with organic solvent component resulting in considerable reduction of the energy cost incurred in the recovery and purification of the organic solvent.

Application of salting in effect: Salting in occurs when, for instance, a polar solvent is added to an aqueous salt solution and is preferentially solvents the water and hence breaks the hydration cages previously formed around the salt ions. The may be used to recover salts from concentrated aqueous solution, and it is also important in biological separation process such as purification of proteins, enzymes, nucleic acids and others.[2]

Application of Salting out effect:

1. Recovery of tightly hydrogen bonded organics from water such as formaldehyde, formic acid and acetic acid by using ionic salt.
2. Biphasic mixtures containing of two immiscible phases are separated by use of salt like ionic salt.
3. Mixture having non polar solvent +polar solvent + water, then salt is used to separate the solution.

1.3 OBJECTIVE OF THE PRESENT WORK

In this project, a suitable correlation was suggested for application in industrial extraction process involving water + solute + solvent + electrolyte systems. The correlation has to be able to give an accurate description of liquid-liquid equilibrium that is important for solvent extraction process. The present system comprises the following components.

Water+1-Butanol+Acetone

The main objective of the present work is to suggest a suitable correlation for the salt effect.

1.4 LIQUID-LIQUID EQUILIBRIUM

Triangular diagrams:

Liquid-liquid extraction involves the use of systems composed of at least three substances, and in most cases all three components appear in both insoluble phases. Ternary systems are often represented on equilateral or right triangular coordinates.

Triangular diagrams (fig. 3) are used for representing three component systems. Every possible composition of the ternary mixture corresponds to a point in the diagram. Each corner of the triangle represents a pure component and its designation is marked at this corner. On the side opposite to this corner the mass fraction of this component is zero. In this diagram the left vortex represent as diluents, right vertex as solvent and the top as solute. The sides of the triangle represent the corresponding two-component system.

The sum of the vertical distances to the three sides from any point within the triangle is also equal to 100 percent, from geometrical considerations.

If the quantities of diluents, solvent and solute present in a ternary mixture are such that two phases exist, each phase is said to be mutually saturated. A plot of the compositions of the two individual phases when in equilibrium with each other gives a mutual solubility curve. Only ternary systems with miscibility gaps are suitable for extraction, and the boundary line between the liquid single-phase region and two-phase region is particularly important. This boundary line is called the binodial curve. Every point in the binodial curve is in equilibrium with another binodial point. The lines, which connect points in equilibrium with one another, are called tie-lines. All mixture, which correspond to a point on the tie line separate into two phases.

1.5 SALT EFFECT ON LLE

Salt has a great effect on LLE. The addition of non-volatile solute to a solvent mixture changes the interaction among the various solvent solutes molecules resulting in shifting their phase equilibrium even to the extent of eliminating the solutrope in LLE. The salt mainly affects the solubility of organic component in an aqueous-organic solvent mixture. Addition of an electrolyte generally salts out the organic solvent molecules thus enriching the organic in organic phase with organic solvent component resulting in considerable reduction of the energy cost incurred in the recovery and purification of organic solvent. The distribution of solute between two liquid phases mainly depends upon the concentration of electrolyte. The electrolyte will remain in the phase in which it is most soluble and the other solute will be transferred to the phase that it is poor in electrolyte. In other cases the addition of salt to a solvent mixture can cause a phase split in a system that did not show demixing, this treatment is sometimes used to enable separation by liquid extraction. Many liquid-liquid system exhibits the solutropy and the phenomena in which the solute favours one phase at low solute concentration other at higher solute concentration. A change in the behaviour of the solutropy system is expected when salt is added in the system.

Selectivity, it is the process of removal of solute preferentially over water, which is significantly affected by the salt present in the system. The selectivity, which is a ratio of distribution coefficient of solute to that of water, is changed much more by salt addition then is the distribution coefficient of the solute alone. The lower distribution coefficient of water can be attributed to the association of water molecule in unextracted slating the aqueous phase, which impedes a transfer of water to the organic phase. From practical point of view resulting higher selectivity means a good separation.

1.6 SALTING OUT & SALTING IN

SALTING OUT:

Salting out can also is explained by the fact that when the ions are solvated, some of the water becomes unavailable for solute which is then salted out from the aqueous phase. This can be exploited to remove organic compounds from water. The term salting out is used since if salt is added to a saturated solution of a non-electrolyte in water, the result is to bring the non-electrolyte out of solution. [2]

SALTING IN:

Salting in occurs when, for instance, a polar solvent is added to an aqueous salt solution and is preferentially solvents the water and hence breaks the hydration cages previously formed around the salt ions. The may be used to recover salts from concentrated aqueous solution, and it is also important in biological separation process such as purification of proteins, enzymes, nucleic acids and others. [2]

CHAPTER - 2

LITERATURE REVIEW

2. EFFECT OF SALT ON LLE

A lot of authors have worked on liquid-liquid equilibrium system. But few of them worked on the salt effect on LLE. It is observed that the use of salt has been proven advantageous. In this review developments and trends are outlined with emphasis on existing correlation. The literature relating to the industrial application with such a salt effect is described.

2.1 Salt effect on LLE

Table-1

Serial number	Literature	System studied	Salt used	Results
1	Hasseine A., Meniai A H, Korichi M, salting out effect of single salt on LLE, science direct, Desalination 242 (2009) pp-264-276 [2]	Water+acetone+tolune Water+cyclohexane+2-propanol Water+xylene+methanol	NaCl, KCl	Salting out effect is more prounced with NaCl compared to KCl, due to difference in hydration energies.
2	Bourayou N., Meniai A H, Influence of salt on liquid phase equlibria for totale miscible organic compound with water, science	Water+acetone Water+propanol	NaCl, $CaCl_2$	The addition of two salts has shifted the systems from being totally homogeneous to heterogeneous one. This has great application in phase

	direct, Desalination 185 (2005) pp-473-481 [4]			separation process.
3	Hu Mancheng, Wang Meixia, Li Shu ni, Jiang Yucheng, Guo Haiyan, LLE for Quaternary systems at 298.1K, science direct,fluid phase Equilibria 263 (2008) pp-109-114. [10]	Water+1-propanol Water+2-propanol	KCl, CsCl	Influences of the inorganic salts and aliphatic alcohols on the LL region, in short, the different salvation abilities and solubilities of KCl, CsCl and the different polarites of the two alcohols affected the results.
4	Chen Jui Tang, Chen Ming-Chung, salting effect on LLE for the ternary system, science direct, Fluid Phase Equilibria 266(2008), pp-1-7. [3]	Water+N-methyl-2-pyrrolidone+1-pentanol	NaCl, KCl, CH3-COOK	The lquid phase splitting for ternary system of water+N-methyl-2-pyrrolidone+1-pentanol can be enhanced by adding the same percentage of salts and the influence follows the order of NaCl>KCl>KAc.
5	Santos G. R,	Water+Ethanol+1-	KBr	The addition of

	d'Avila S.G, Aznar M., salt effect on LLE, Brazilian journal of chemical engineering, Vol. 17, (2000),pp-721-734. [11]	Pentanol		bromide potassium improves ethanol extraction by means of 1-pentanol. The improvement result from salt effect, which modifies the phase equilibrium of the mentioned system, increasing the distribution coefficient for ethanol and selectivity of the solvent.
6	Tan T.C., Kannangare k.K.D.D.S., Liquid-liquid equilibrium of a system in prence of salt, science direct, fluid phase Equilibrium 190 (2001) pp-179-189. [12]	Water+1-propanol Water+1-propanol+methyl-ethyl-ketone	KCl	Although methyl ethyl ketone is a reasonably good solvent for solvent extraction of 1-propanol from its aqueous mixture, its extractive effiency can be further and considerably enhanced with

				the addition of KCl into the solvent mixture.

Serial number	Literature	System studied	Salt used	Results
7	Solimo Horacio N., Bonatti Carlos M., Zurita Jose L., de Doz Monica B. Gramajo, salt effect on LLE,Elsevier, Fluid-Phase Equilibria137 (1997) pp-163-172. [13]	Water+propanic acid+1-butanol.	NaCl	The presence of the salt decreases the solubility of the system, increasing the heterogeneous zone. The experimental results lead to the conclusion that a salting-out effect is present at all studied NaC1 concentrations, increasing for

				higher salt concentrations.
8	R. Pedraza, F. Ruiz, M.D. Saquete, V. Gomis,Liquid-liquid-solid equilibrium for quaternary system,Science direct, Fluid Phase Equilibria 216 (2004) 27–31. [14]	Water+1-butanol+2 salts	NaCl, KCl	The liquid–liquid tie lines obtained have been used to check the accuracy of the predictions using the electrolyte NRTL model (MNRTL). The model is useful for the calculation of the liquid–liquid equilibrium data of quaternary systems using parameters obtained by correlation of some Of the ternary systems that constitutes it.
9	Tan T.C., Aravinth S., Salt effect on LLE, Elsevier, Fluid Phase Equilibria	Water+acetic acid+1-butanol	NaCl, KCl	Both sodium and potassium chloride increased the

	163(1999).243–257. [15]			area of the two-phase region and decreased the Mutual solubilities of 1-butanol and water. Both marginally decreased the concentration of 1-butanol and acetic acid in the aqueous phase while significantly increased their concentrations in the organic Phase.
10	Vakili-Nezhaad G.R., Mohsen-Nia M.,Taghikhani V., Behpoor M., Aghahosseini M., Salting out effect of salts on ternary LLE data, Science direct, J. Chem.Thermodynamics 36 (2004) 341–348. [7]	(water+propionic acid+isopropyl methyl ketone) (water+propionic acid+isobutyl methyl ketone)	NaCl, KCl	The results showed that the electrolytes significantly affect the solubility of Propionoic acid In the organic solvents used. The results also showed that the distribution

				coefficients for Propionoic acid and the selectivity of the organic solvents in extracting Propionoic acid increase in the presence of electrolytes in the ternary systems.

2.2 SYSTEM STUDIED UNDER PRESENT WORK

Literature	System Studied	Salt Used	Remarks
Santos Fania S., d'Avila Saul G., Aznar Martin, salt effect on liquid-liquid equilibrium of water + 1-butanol + acetone: experimental determination and thermodynamic modeling, science direct, fluid phase equilibria 187-188 (2001) 265-274.[6]	Water+1-Butanol+Acetone	NaCl, CH_3-COONA	Electrolyte LLE data of quaternary systems at 20 and 40^0c or experimentally determined by chromatographic and gravimetric analysis .the effect of the salt addition on the original ternary system was observed by the increase of two phase region and the changes in the slope of the experimental tie lines.

CHAPTER - 3

EXPERIMENTAL PROCEDURE AND SET UP

3. INTRODUCTION

The experimental measurement of liquid-liquid equilibrium must achieve two things.

- It must locate the position of the solubility curve and
- It must determine the composition of the coexisting phases, which locate the ends of the tie lines.

In some cases these two objectives can be achieved in one measurement, and in other cases, two sets of measurement are necessary. In the first case, for a ternary system mixtures of three component are allowed to separate into its conjugate phases at equilibrium and the equilibrate layers are analysed for their composition which will give the end points of the tie lines. These end points when connected will give the binodial curve. This method is called the method of analysis. The second method involves the estimation of binodial curve and the tie lines in two stages, which is measured separately. [18, 21]

3.1 Materials Used:

Chemicals and salts used:

- 1-Butanol
- Acetone
- Water
- Anhydrous NaCl (dried)
- Anhydrous KCl (dried)

3.2 PHYSICAL PROPERTIES OF SOLVENT USED

Components	Boling point (^{0}C)	Melting point(K)	Molecular Wt.(gm)	Density(Gm/ml)
Acetone	56.53	178	58.08	0.79
1-Butanol	117	183	74.12	0.81
Water	100	273	18.015	1

3.3 EXPERIMENTAL SET UP

Experimental set up used for the determination of solubility data and tie line determination.

Apparatus required:

- Jacketed burette
- LLE apparatus
- Magnetic stir bar
- Thermometer
- Syringe
- Refractometer

Jacketed Burette:

A Pyrex 50ml burette, provided with a jacket for water circulation from the thermostat was used for titration in the determination of solubility data.

LLE apparatus:

It is jacketed cell water is flowing in the jacketed portion to maintain a constant temperature for proper working of reaction. A thermometer is inserted in the inner cell to measure the temperature. The prepared solution is fed into the inner cell, where it under goes proper mixing with salt in presence of a magnetic stir bar.

Magnetic stir bar:

It is used for proper mixing of salt and prepared solution in the presence of magnetic field in the inner cell. The stirring is continued for 2 to 3 hours.

Thermometer:

It is a mercury glass thermometer. It is used to measure the temperature of water in the inner cell.

Syringe:

It is used to draw liquid phase sample from the opening at the top sampling port to avoid cross contamination by other phase during the sampling process.

Refractometer:

It is used for the measurement of composition of phases at equilibrium.

3.4 PROCEDURE FOR SOLUBILITY DATA FOR TERNARY LIQUID SYSTEM:

A known quantity of a heterogeneous mixture (water varying from 1 to 20ml and the solvent varying from 20 to 1ml) was taken in a 100ml jacketed cell. Then the mixture was titrated with solute (acetone) taken in a jacketed burette. Water from the constant temperature bath was circulated through the jacket. The mixture was kept in constant stirring condition. The point of miscibility was noted. The end point, in this case, the disappearance of turbidity was noted. Then the refractive index of the mixture was measured by refractometer. The mass fraction of each component was calculated and tabulated. The above procedure was repeated for other specific mixture so as to cover entire range of composition. [18, 21]

3.5 SOUBILITY DATA FOR SALT CONTAINING TERNARY LIQUID SYSTEMS:

The solubility data of a salt containing ternary system was determined by adopting the same experimental procedure used for salt free system, except that water was replaced by aqueous salt solution. The concentration of aqueous salt solution was varied from 5% to 15% of salt by mass; these concentrations were below saturation with respect to water. The solubility curve near the solvent rich region resulted in the precipitation of salt, which marked the disappearance of turbidity. Hence a complete solubility curve could not be obtained for the entire range of composition for the systems under this study. [18, 21]

3.6 MEASUREMENT OF EQUILIBRIUM DATA FOR LIQUID MIXTURE WITH AND WITHOUT A SALT:

A known heterogeneous ternary mixture was prepared by taking predetermined quantities of the three components (10ml solvent + 10ml diluents (water or salt solution of known concentration) + 1ml to 30ml of solute) in a 100ml jacketed cell. The mixture was thoroughly agitated for two hours by magnetic stirrer. After agitation, the mixture was allowed to stand for 2 hours to attain equilibrium. Two phases were found (i.e. reffinate & extract). The individual layer are separated by syringe and weighed. Then the refractive index of each layer was measured. In the case of dissolved salt each layer were boiled separately and condensed to make salt free and the refractive index of each layer were measured. The same technique was repeated for other known heterogeneous mixture. [18, 21]

3.7 METHOD OF ANALYSIS

There are many method used for analysis of equilibrium composition for ternary liquid liquid equilibrium system. These are as follows:

1. Titration method
2. Refractive index method
3. Gas chromatograph method
4. Specific gravity method

Refractive index method:

Equilibrium data of LLE for three components system is obtained by measuring refractive index of the solution using refractometer.

To find equilibrium data, known amount of three components corresponding to points within the binodial curve contained in stopper flasks, were agitated in the constant temperature bath over a period of 3 hours. At the end of this period the flasks were allowed to remain the bath until the phases had completely separated. The samples of the separated layers were withdrawn and their refractive indexes were measured. The composition of the equilibrium layers were found by references to a large scale plot of refractive index against solute concentration for saturated solution. In the case of dissolved salt each layer were boiled separately and condensed to make it salt free and then refractive index of each layer was measured.

CHAPTER - 4

4. PRESENTATION OF RESULTS

This section represents the result of experimental work done. The solubility data with and without salt determined for above system are presented in table (4.1) as well as plotted in figure. The figures represent the smoothed values of solubility composition. The equilibrium tie line data are also presented in table (4.2). All salt containing data are reported on salt free basis. The experimental tie line data under no salt condition were determined and presented in their respective tables.

4.1EMPIRICAL CORRELATION OF SALT EFFECT ON LLE

The effects of salt on LLE of a ternary system have been widely studied. A lot of theories have advanced to explain the complex effect. However, the mathematical characterization of the salt effect has been semi quantitative at best, because of limitation of theories or inadequacy of assumptions made in the derivation of those equations. Hand and Othmer Tobias [16] have proposed equations to correlate tie line data of ternary liquid-liquid system under no salt condition. Setchenow, Eisen and Joffe [17] have proposed semi empirical models to correlate the tie line data of the ternary LLE under salt dissolved in the system.

Setchenow [25] has proposed the following empirical equation for the salt effect on the distribution of solute between the relatively insatiable systems.

$$\mathrm{Ln}(X^0_{CA}/X_{CA}) = K_S\, X_{SaA} \quad \text{------------ (4.1)}$$

Where, K_S is a salt parameter.

According to Long and McDevit [21] have suggested the following equation which was derived on the basis of thermodynamic consideration

$$\mathrm{Ln}\ (X^0_{CA}/X_{CA}) = K_S\, X_{SaA} + K_C(X_{CA} - X^0_{CA}) \quad \text{---------- (4.2)}$$

Hand's equation [18, 20, and 24] for no salt condition is

$Ln(X_{CB}/X_{BB}) = B\ Ln(X_{CA}/X_{AA}) + Ln\ A$ --------------- (4.3)

Eisen-Joffe [17, 20, and 24] equation is best on the adaptation of Hand's equation to system containing dissolved salts. In their model they have fitted Hand's constants Ln A and B in the following relations in the presence of salt, as a linear function of salt concentration.

$Ln\ A = a + b\ X_S$ and $B = c + d\ X_S$ -------------------- (4.4)

With the above relationships they have modified Hand's correlation into the following expression to suit the salt system. [20]
$Ln\ (X_{CB}/X_{BB}) = (a + b\ X_S) + (c + d\ X_S)\ Ln\ (X_{CA}/X_{AA})$ ------ (4.5)

Where a, b, c and d are constants which depend on the nature of the system, nature of the salt and temperature, but are independent of salt concentration.
Recently Campbell [18, 23] proposed a correlation of ternary liquid system containing dissolved salts. The equation is as follows.

$Ln\ (X_{CB}) = (a + b\ X_S) + (c + d\ X_S)\ Ln\ (X_{CA})$ ------------------ (4.6)

The present system is correlated by using Eisen - Joffe equation and Campbell equation for different salt concentration.

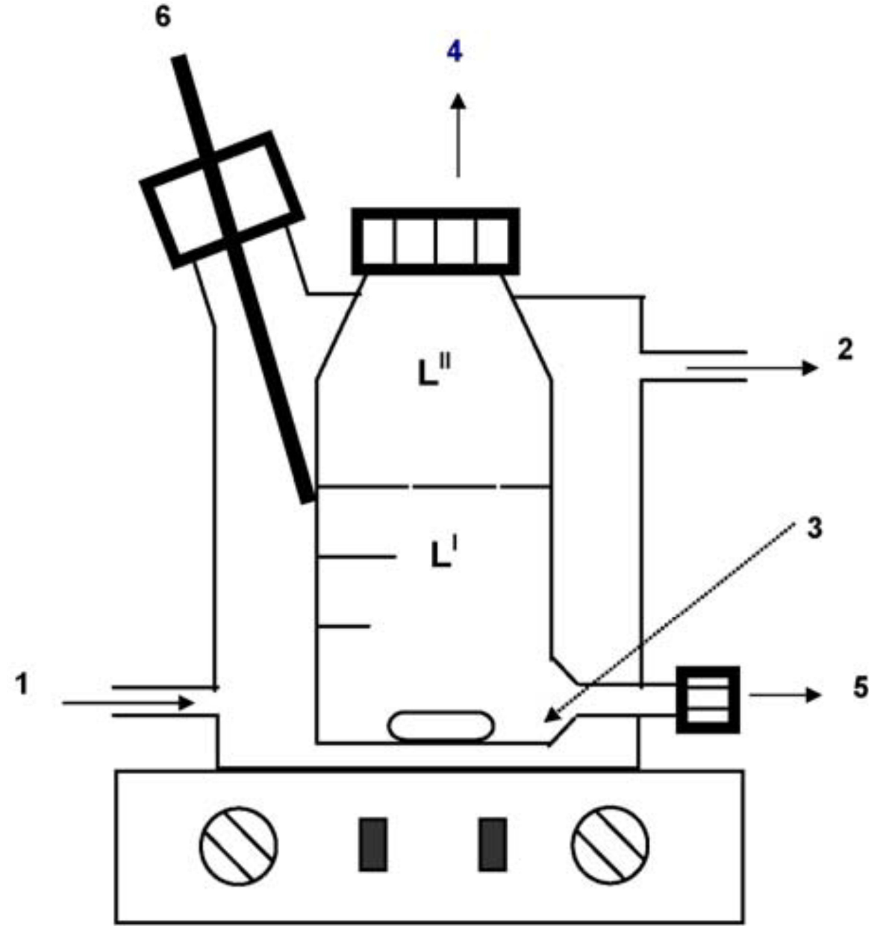

Fig. 1 SCHEMATIC DIAGRAM OF LIQUID-LIQUID EQUILIBRIUM APPARATUS [9]

(1) Thermostatic water inlet
(2) Thermostatic water outlet
(3) Stir bar
(4) Sampling port for upper phase (LII)
(5) Sampling port for lower phase (LI)
(6) Thermometer

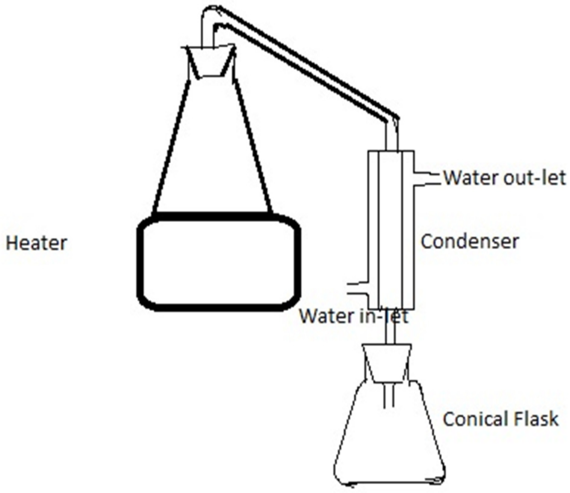

Fig. 2 SCHEMATIC DIAGRAM FOR EVAPORATION OF LIQUID MIXTURE

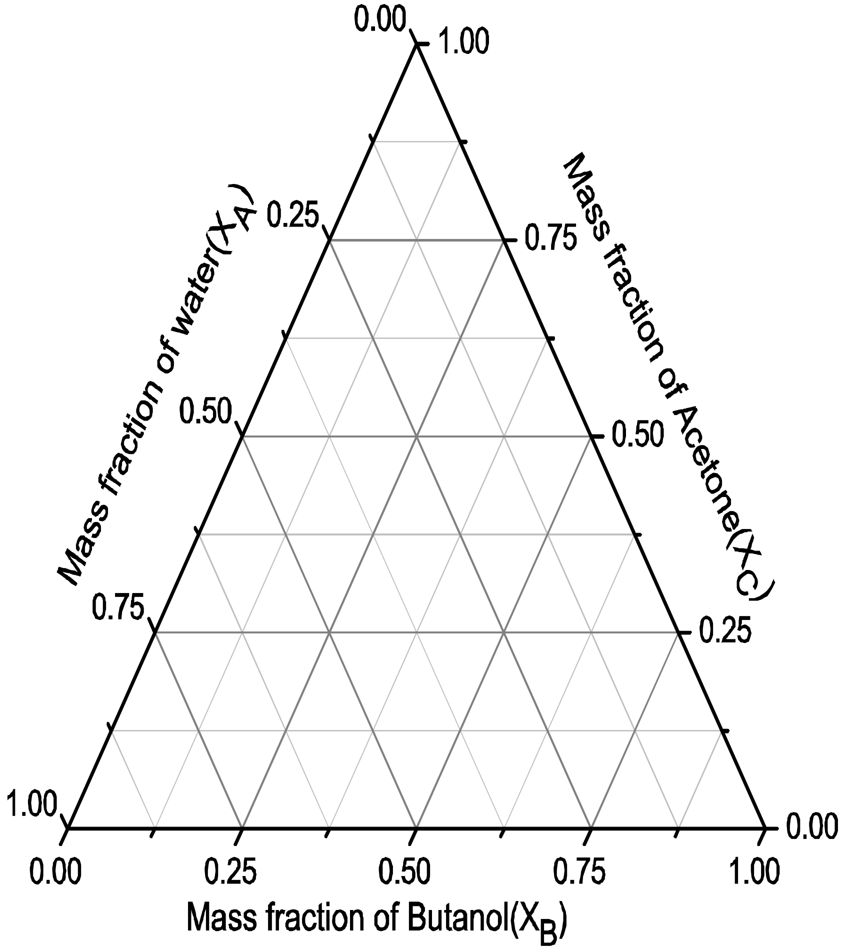

Fig. 3 Triangular Diagram

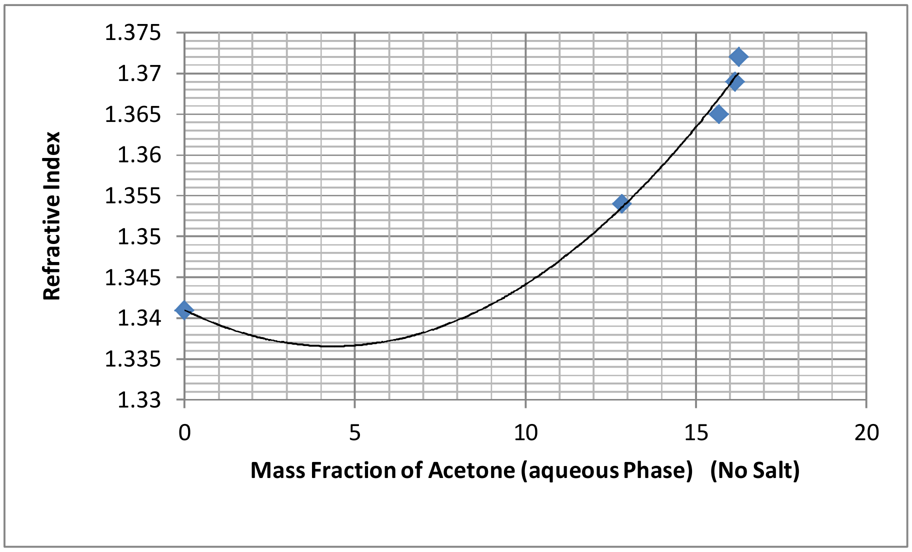

Fig. 4 Mass Fraction vs. Refractive Index (Aqueous Phase) (No Salt)

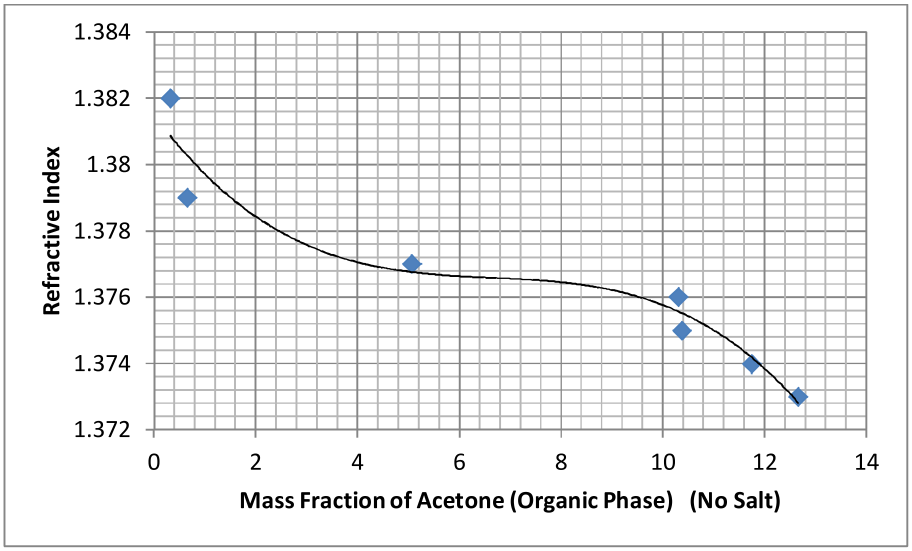

Fig. 5 Mass Fraction vs. Refractive Index (Organic Phase) (No Salt)

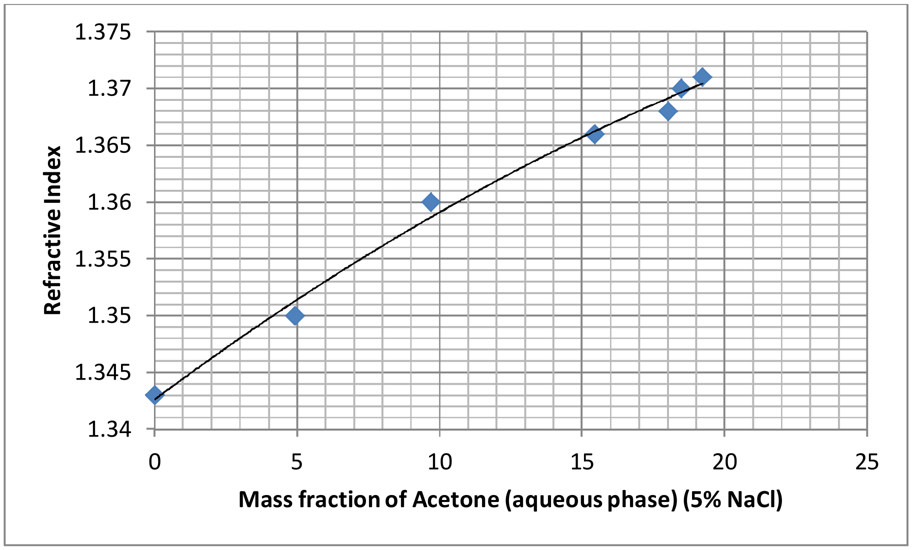

Fig. 6 Mass Fraction vs. Refractive Index (Aqueous Phase) (5% NaCl)

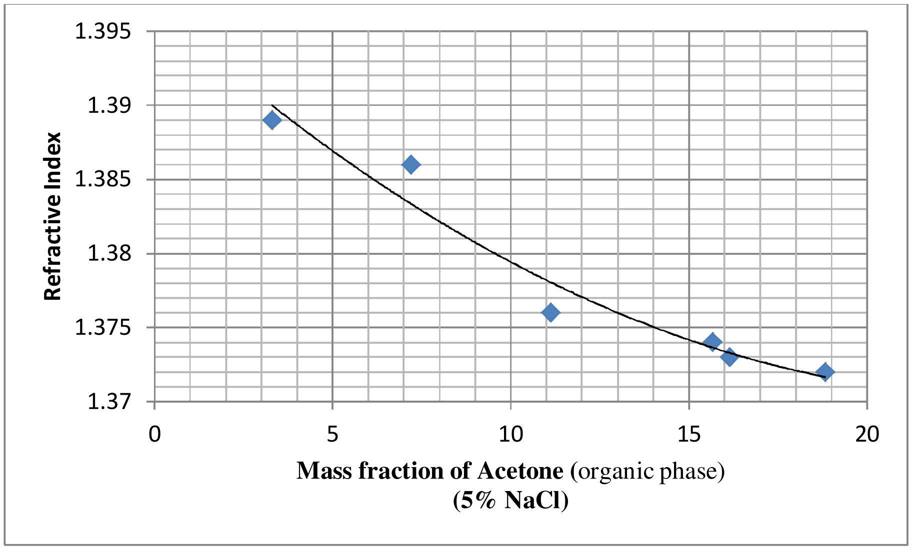

Fig. 7 Mass Fraction vs. Refractive Index (Organic Phase) (5% NaCl)

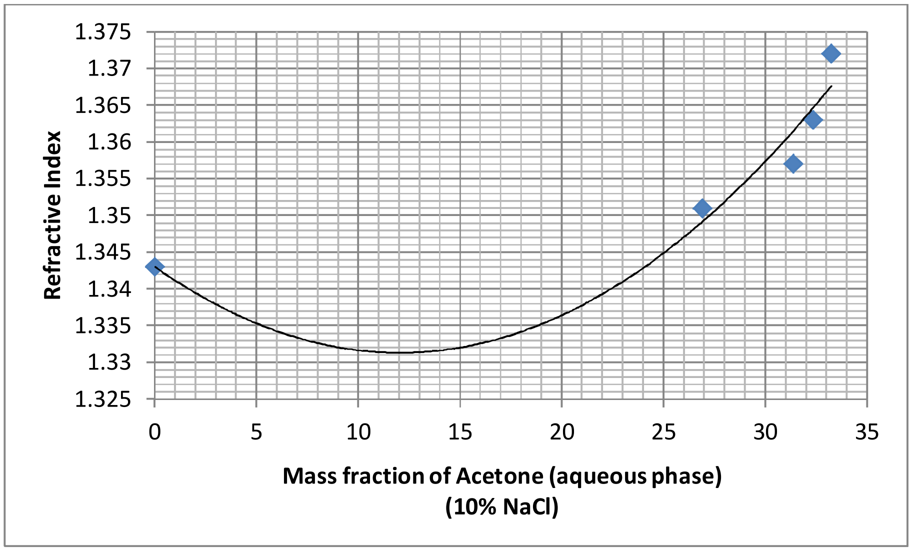

Fig. 8 Mass Fraction vs. Refractive Index (Aqueous Phase) (10% NaCl)

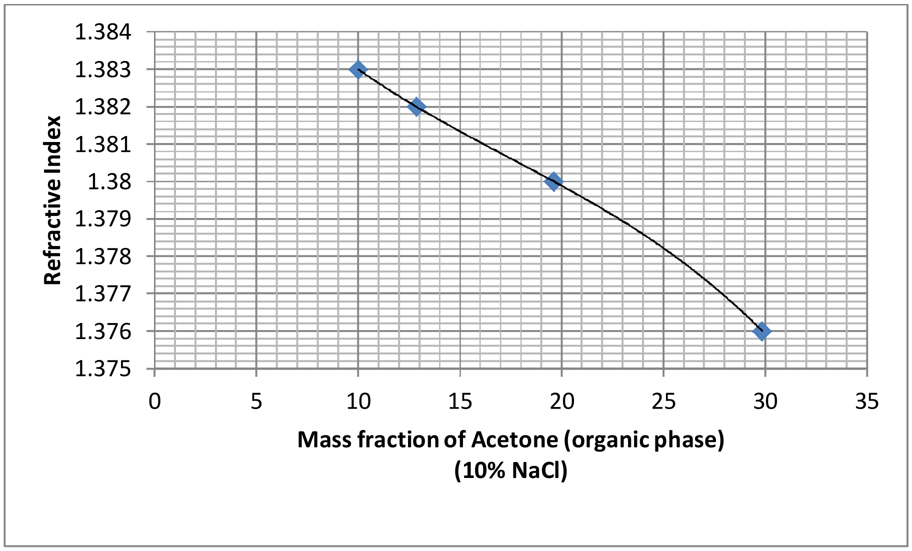

Fig. 9 Mass Fraction vs. Refractive Index (Organic Phase) (10% NaCl)

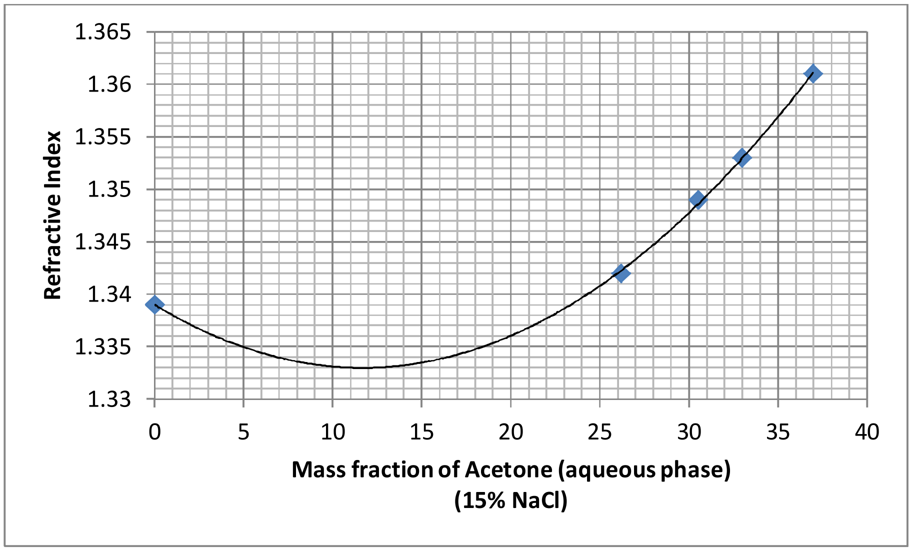

Fig. 10 Mass Fraction vs. Refractive Index (Aqueous Phase) (15% NaCl)

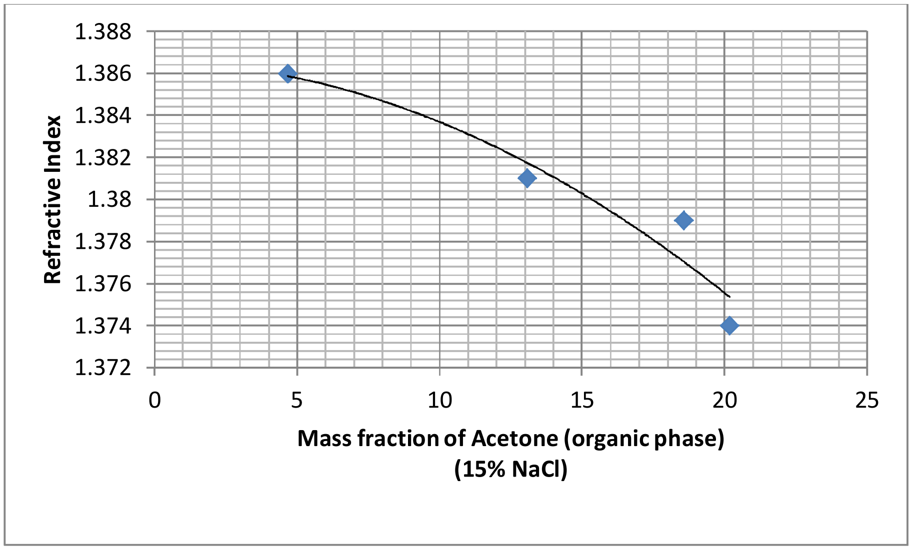

Fig. 11 Mass Fraction vs. Refractive Index (Organic Phase) (15% NaCl)

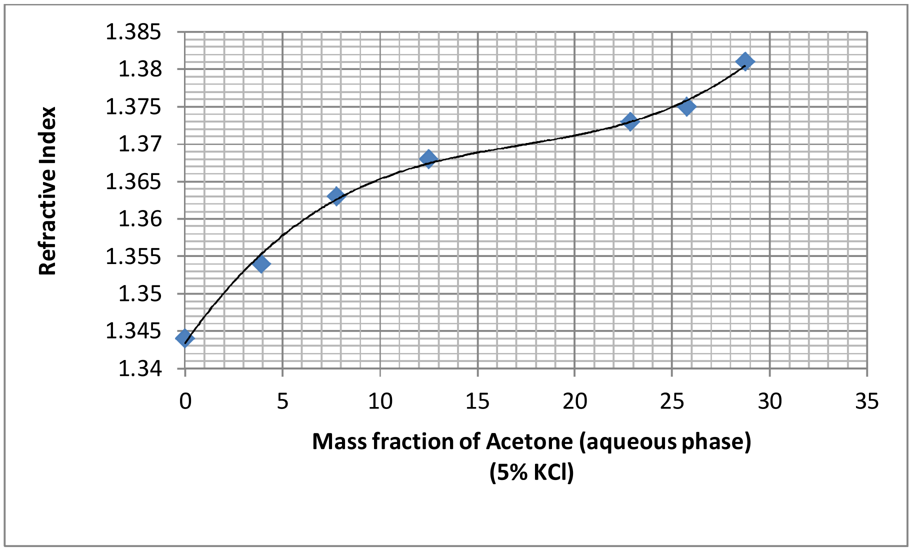

Fig. 12 Mass Fraction vs. Refractive Index (Aqueous Phase) (5% KCl)

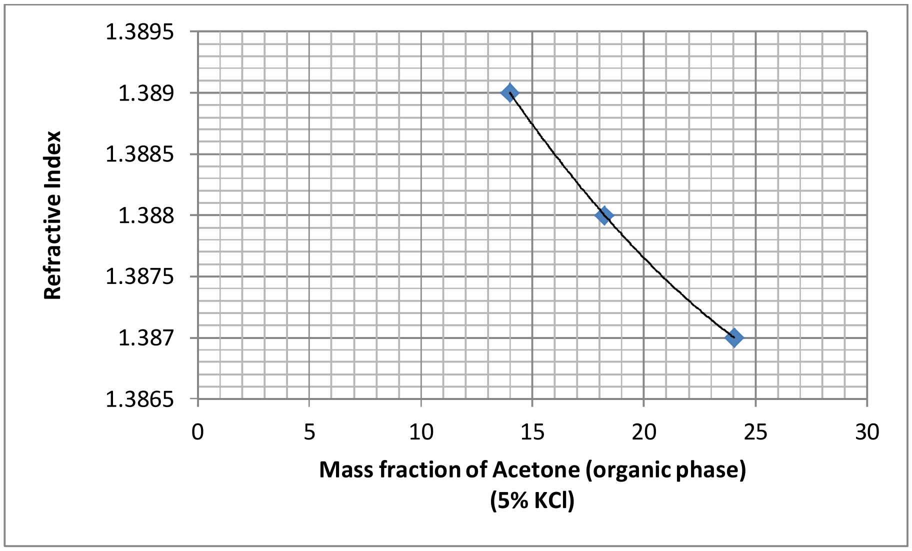

Fig. 13 Mass Fraction vs. Refractive Index (Organic Phase) (5% KCl)

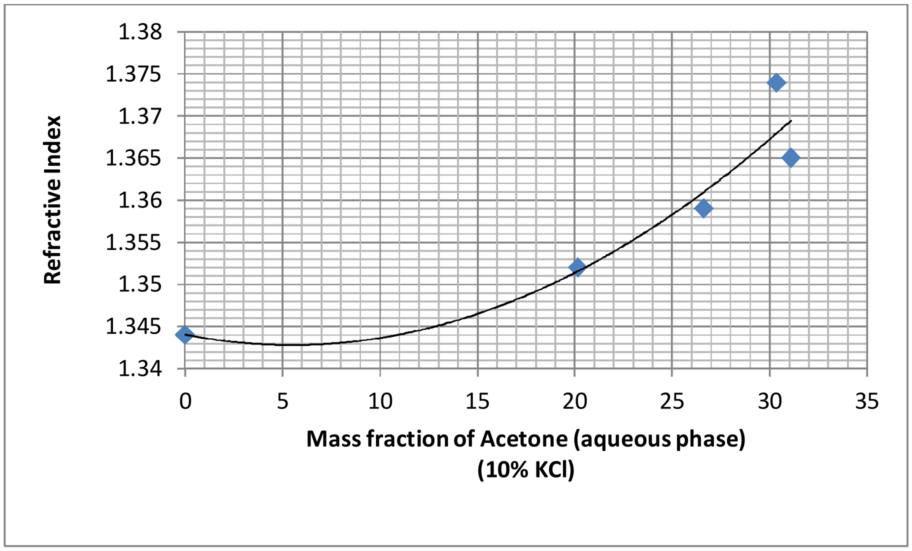

Fig. 14 Mass Fraction vs. Refractive Index (Aqueous Phase) (10% KCl)

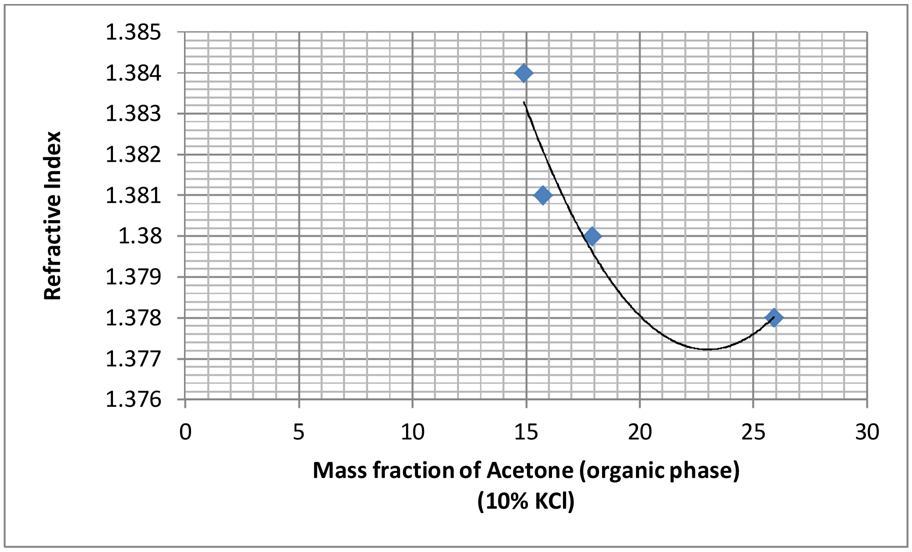

Fig. 15 Mass Fraction vs. Refractive Index (Organic Phase) (10% KCl)

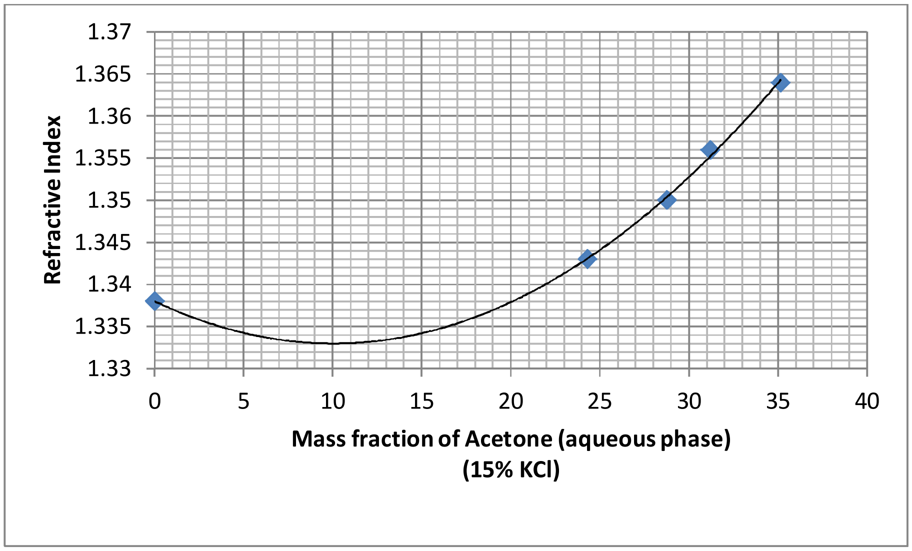

Fig. 16 Mass Fraction vs. Refractive Index (Aqueous Phase) (15% KCl)

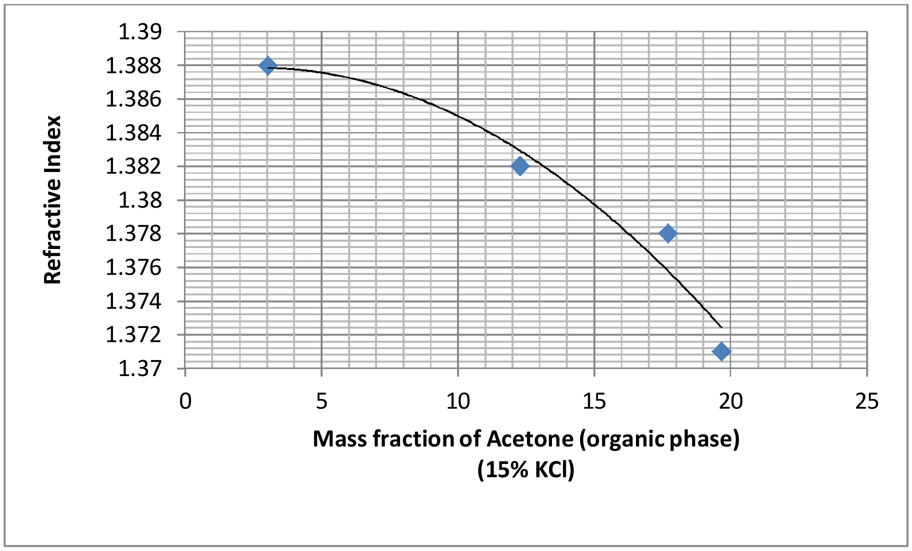

Fig. 17 Mass Fraction vs. Refractive Index (Organic Phase) (15% KCl)

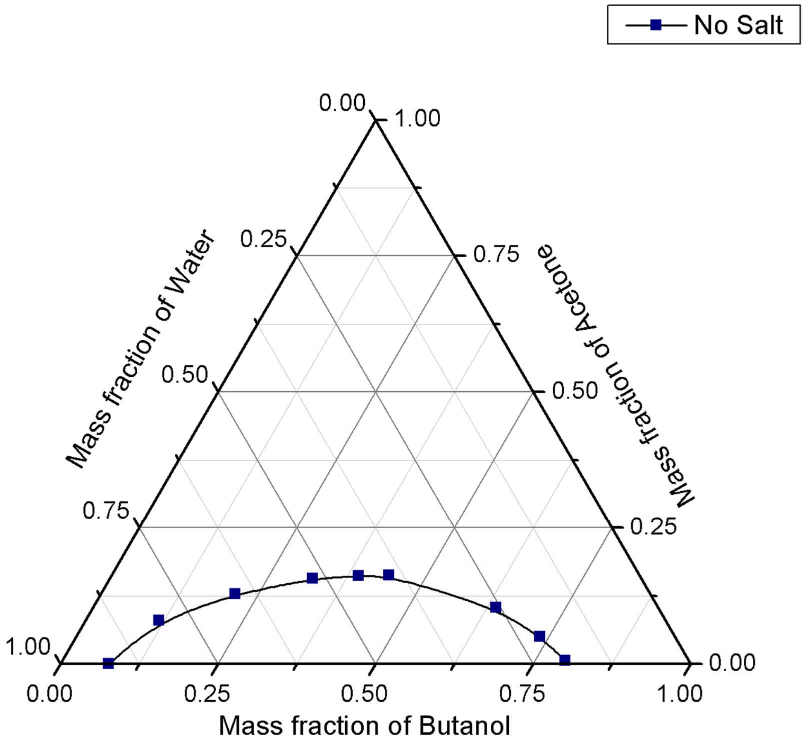

Fig. 18 Solubility curve for no salt

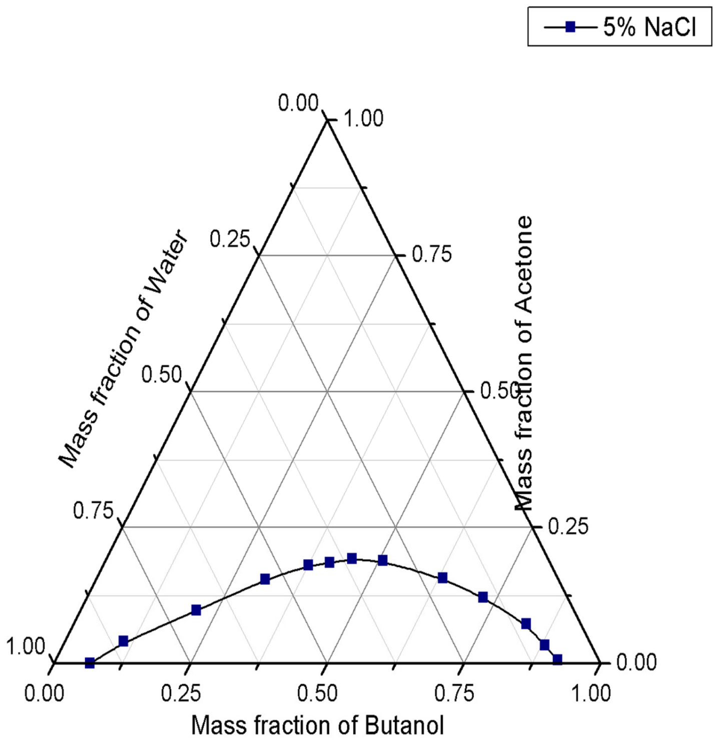

Fig. 19 Solubility curve for 5% NaCl

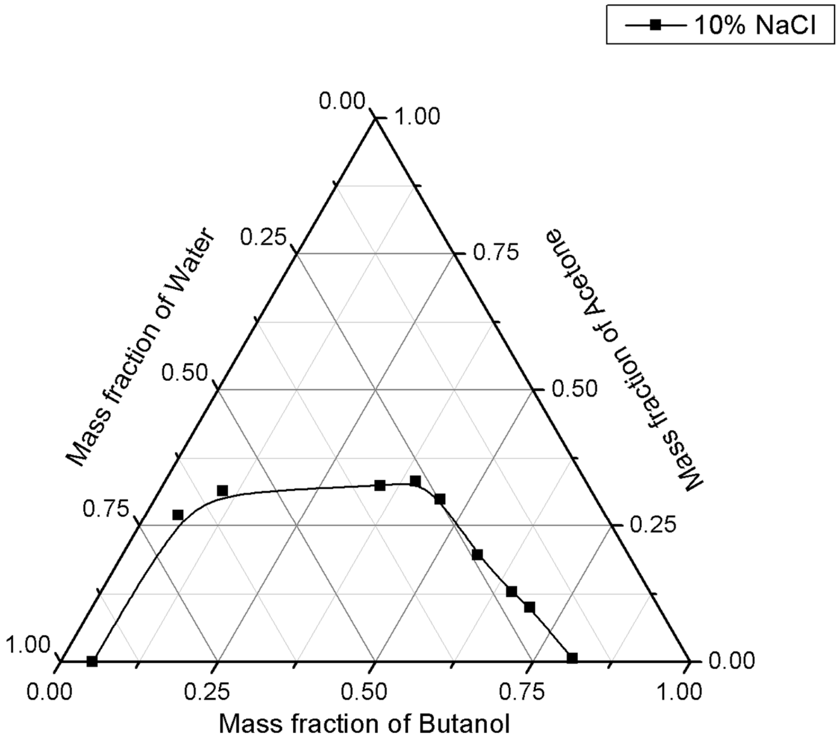

Fig. 20 Solubility curve for 10% NaCl

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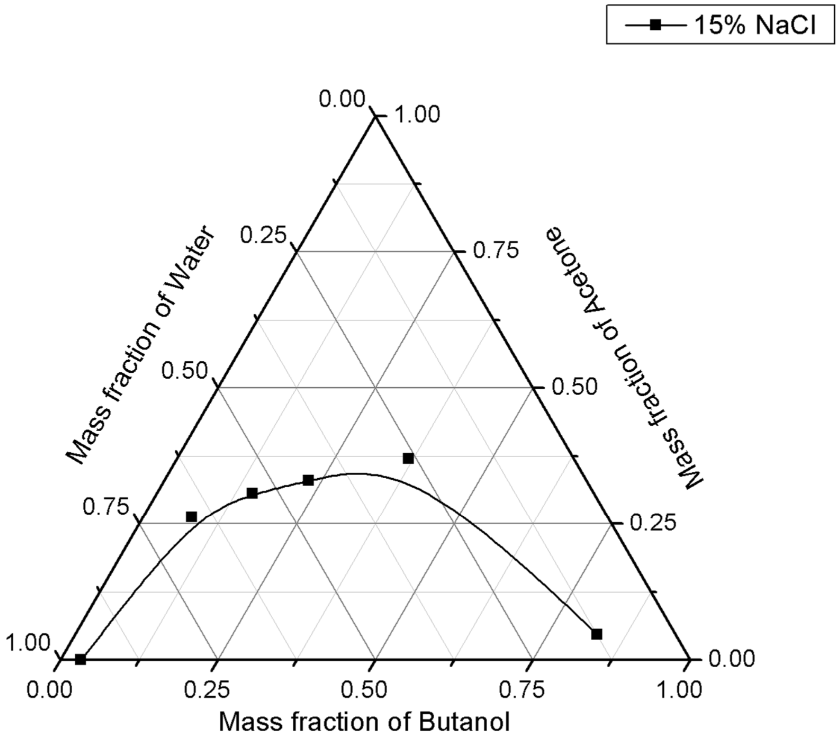

Fig. 21 Solubility Curve for 15% NaCl

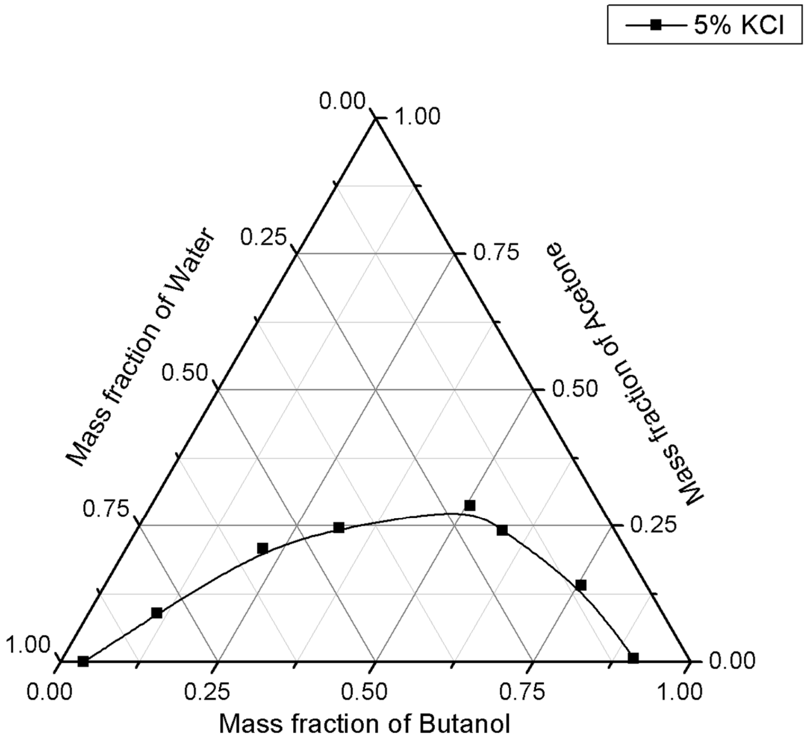

Fig. 22 Solubility curve for 5% KCl

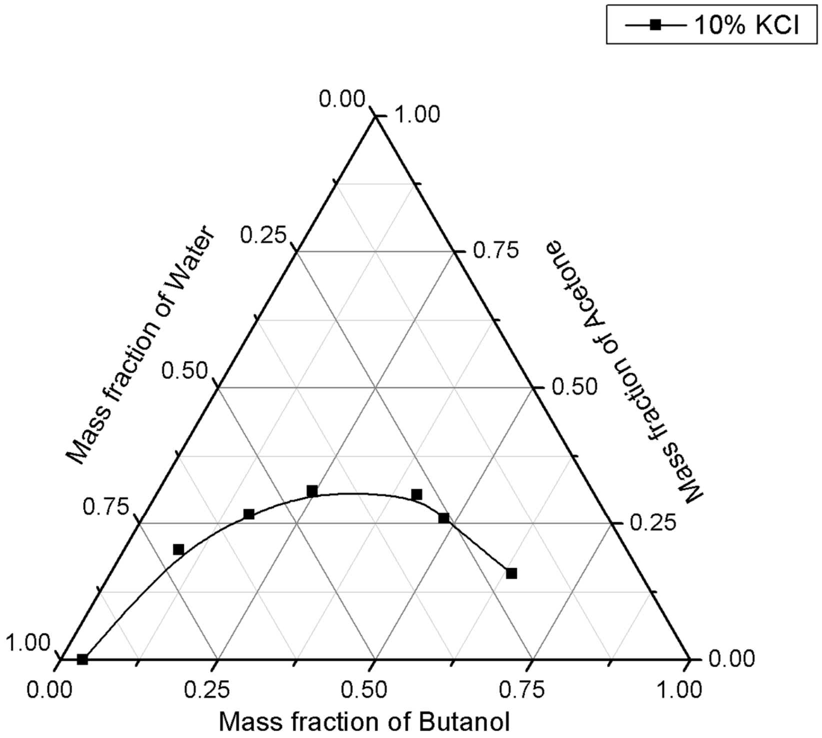

Fig. 23 Solubility Curve for 10% KCl

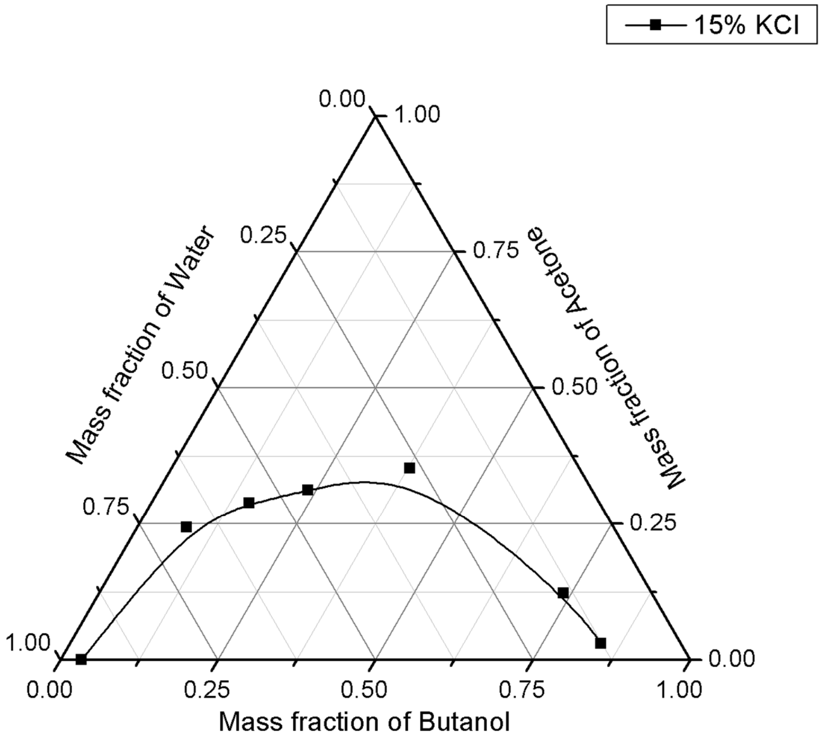

Fig. 24 Solubility Curve for 15% KCl

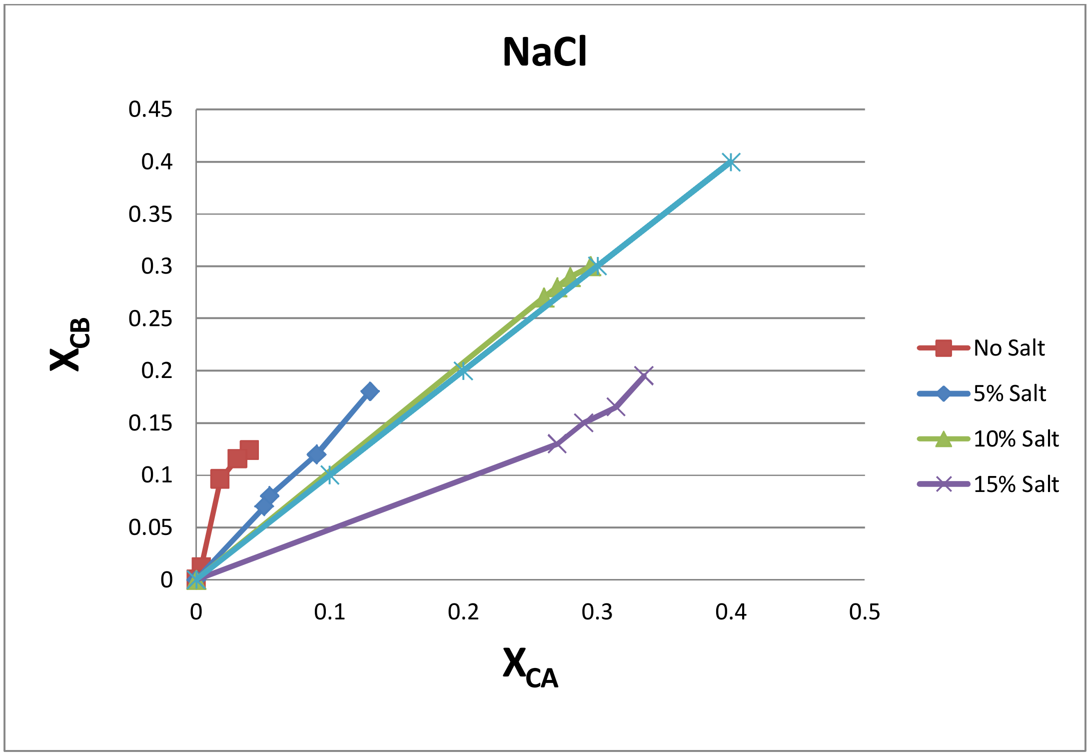

Fig. 25 DISTRIBUTION CURVE

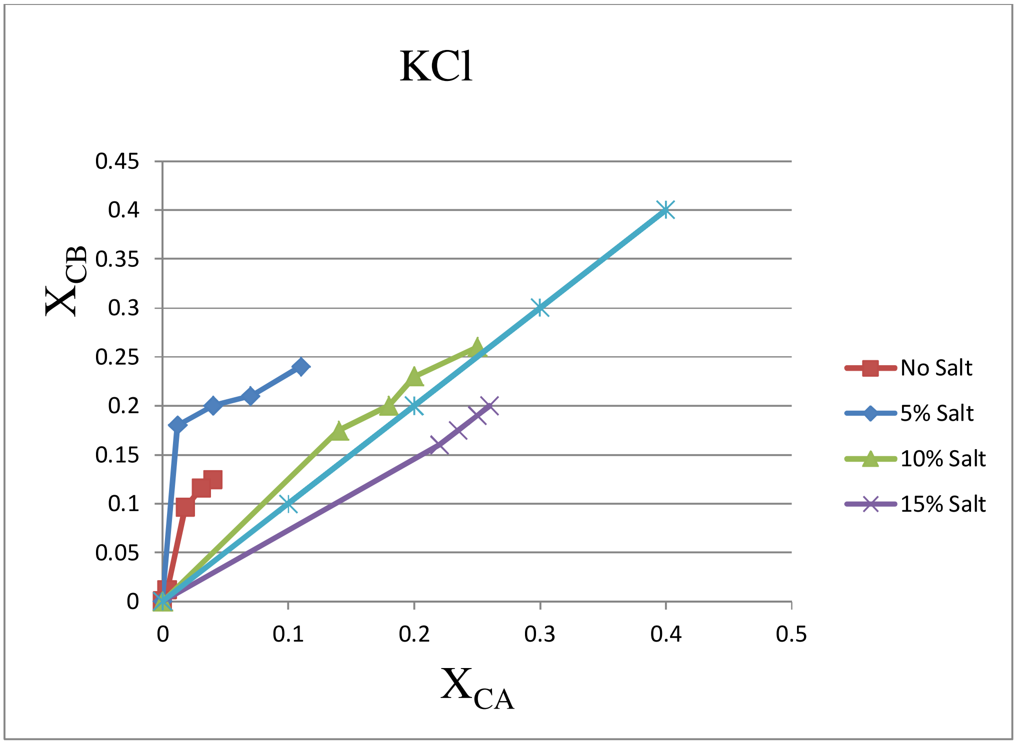

Fig. 26 DISTRIBUTION CURVE

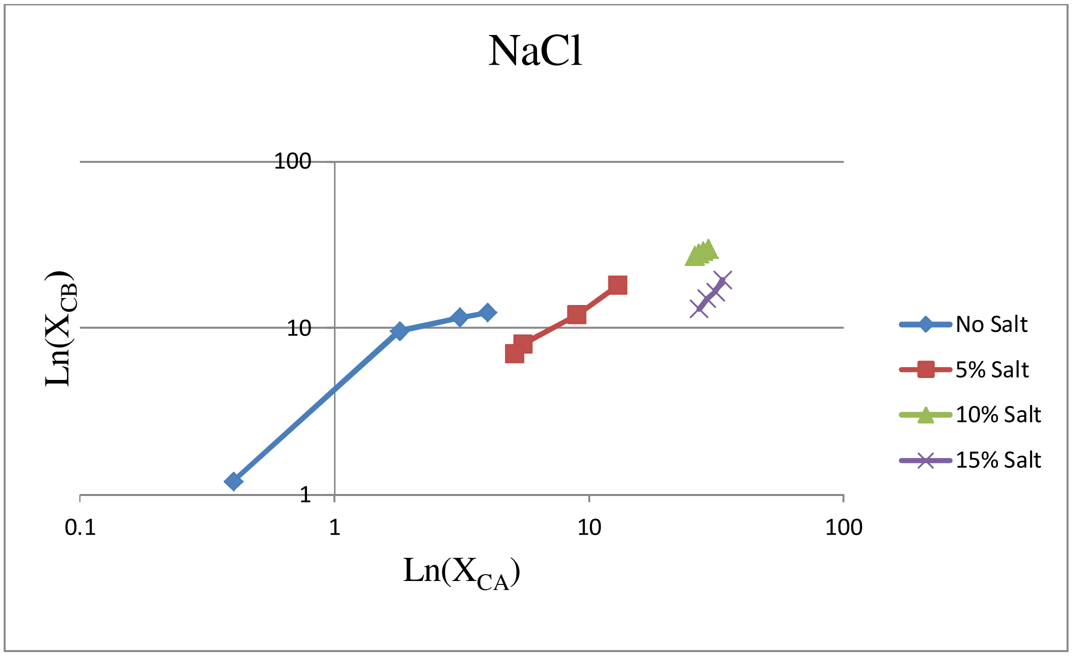

Fig. 27 Campbell's Plot

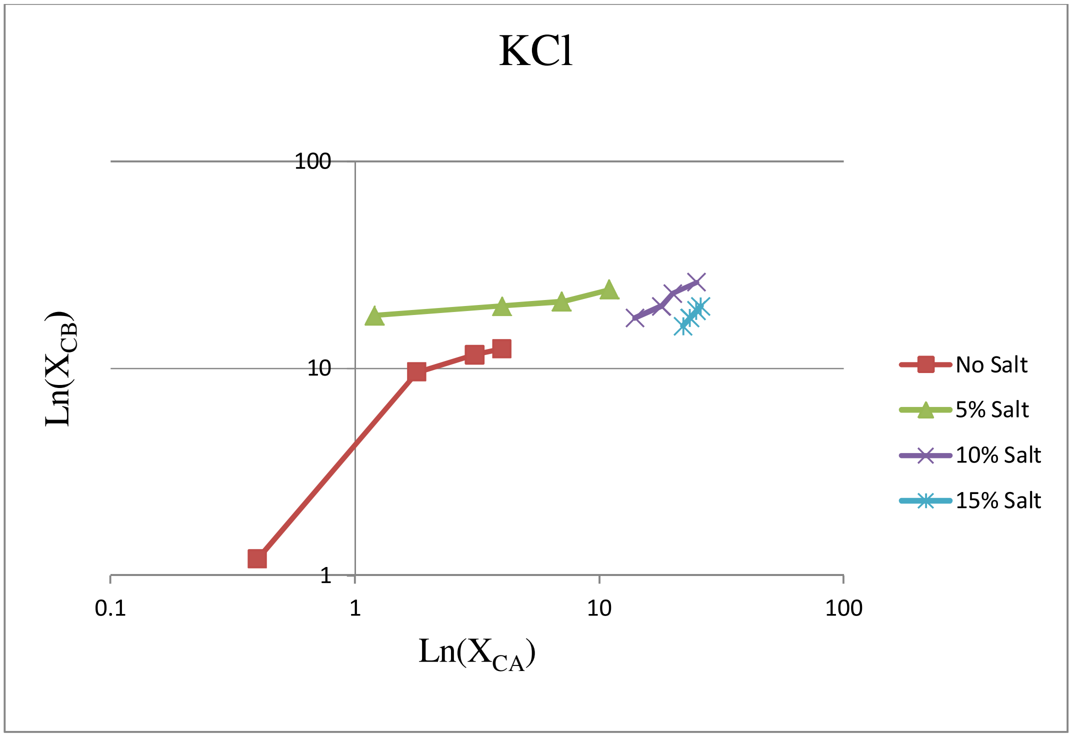

Fig. 28 Campbell's Plot

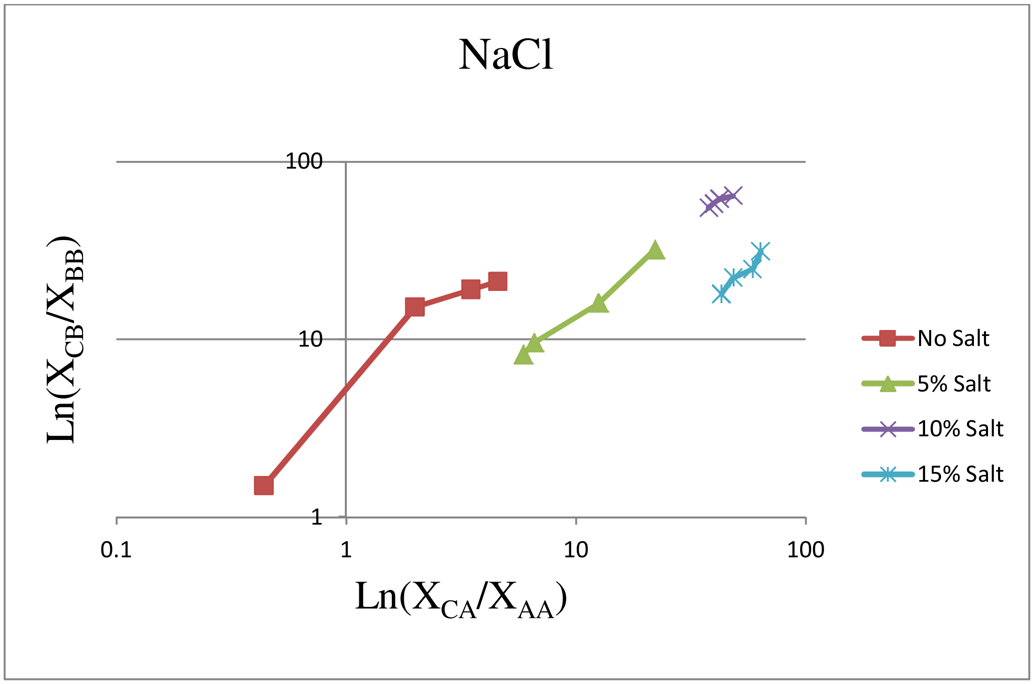

Fig. 29 Hand's Plot

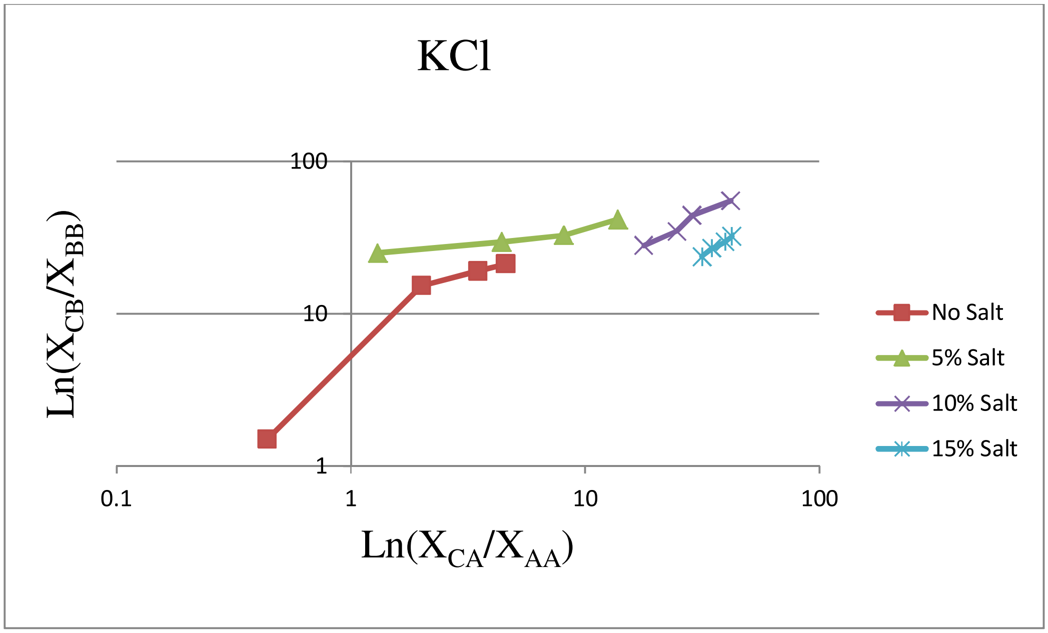

Fig. 30 Hand's Plot

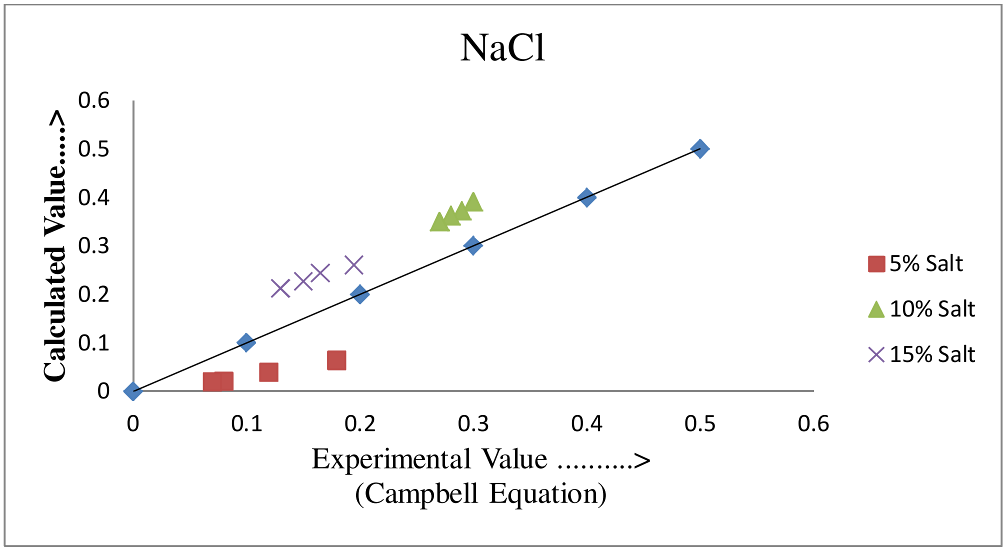

Fig. 31 Experimental vs. Calculated values of mass fraction of acetone (for NaCl)

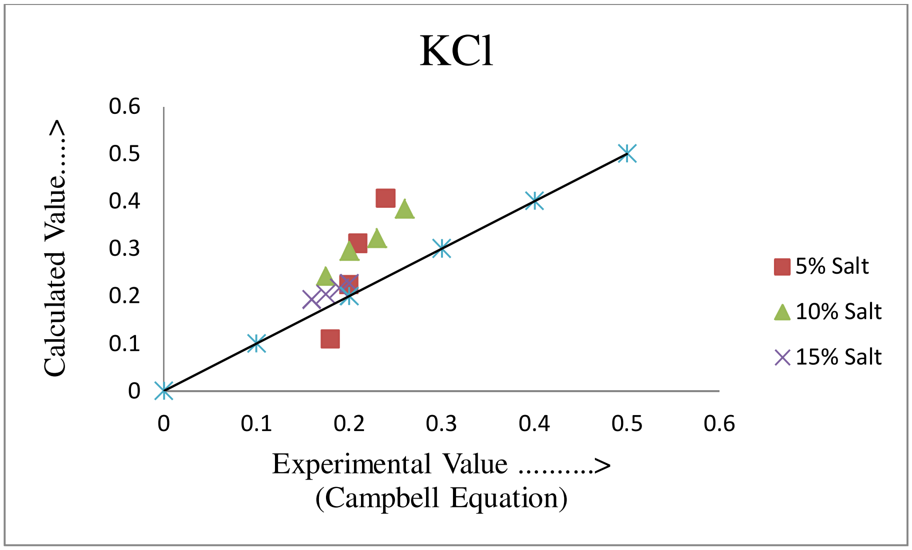

Fig. 32 Experimental vs. Calculated values of mass fraction of acetone (for KCl)

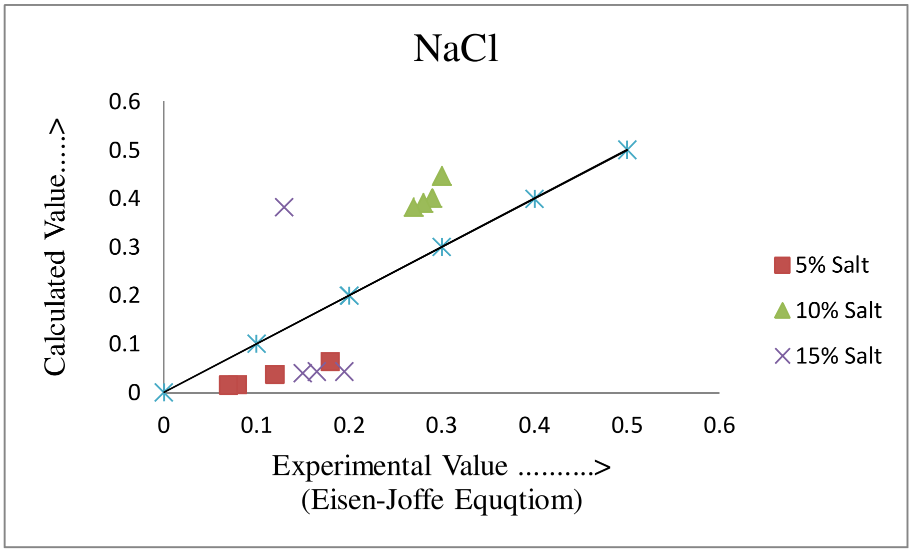

Fig. 33 Experimental vs. Calculated values of mass fraction of acetone (for NaCl)

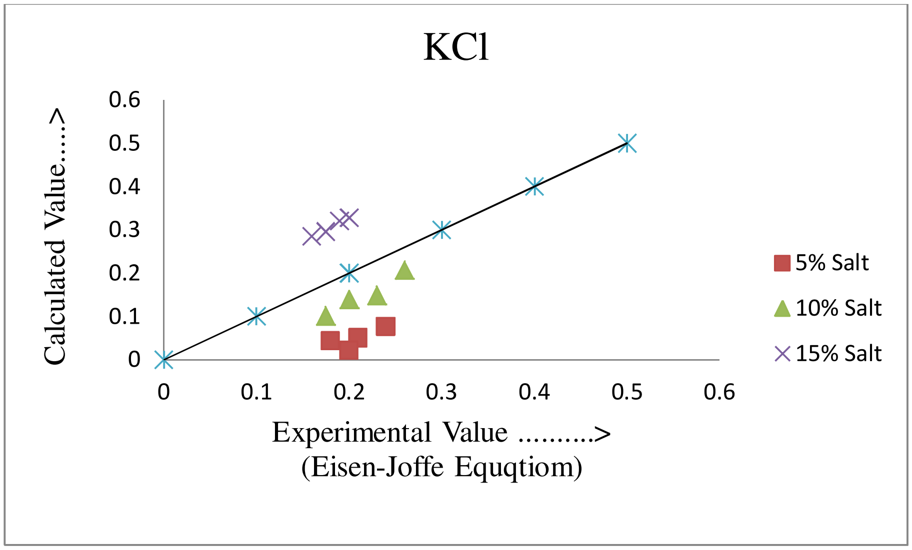

Fig. 34 Experimental vs. Calculated values of mass fraction of acetone (for KCl)

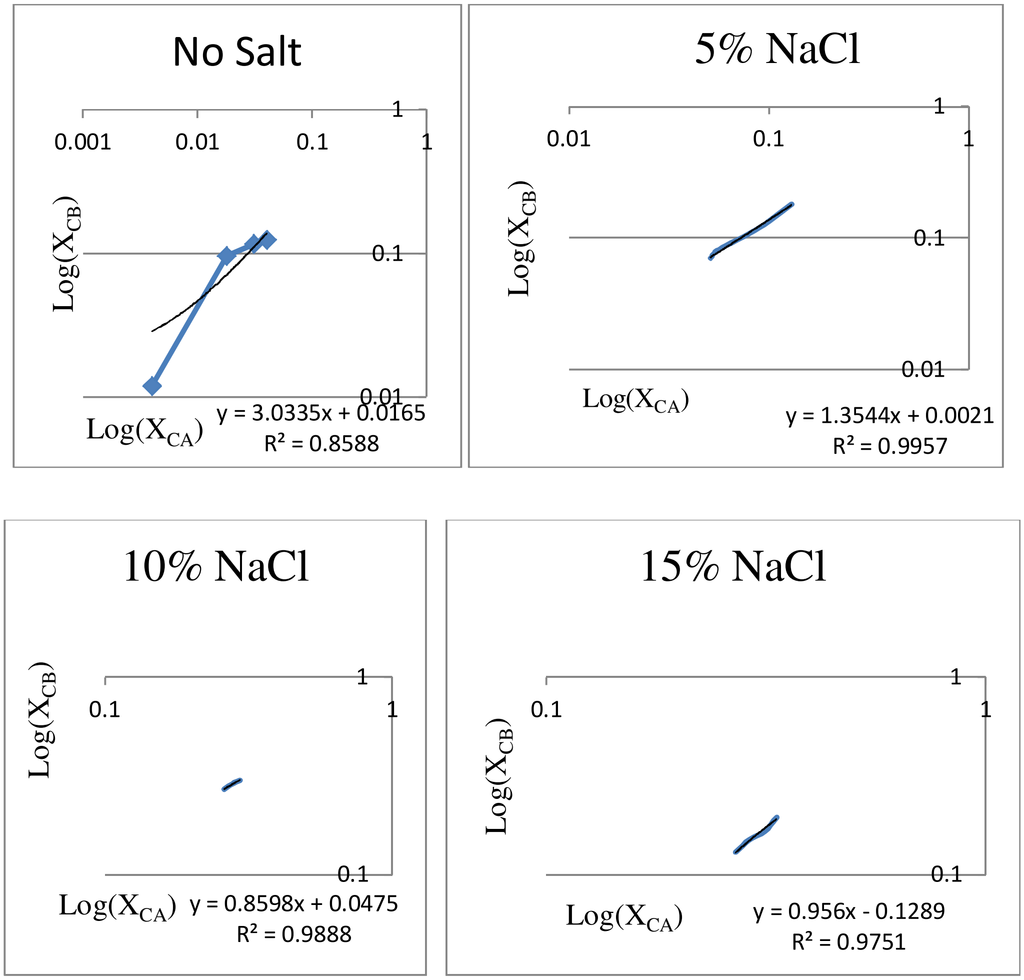

Fig. 35 Determination of Log A & B for NaCl (Campbell Equation)

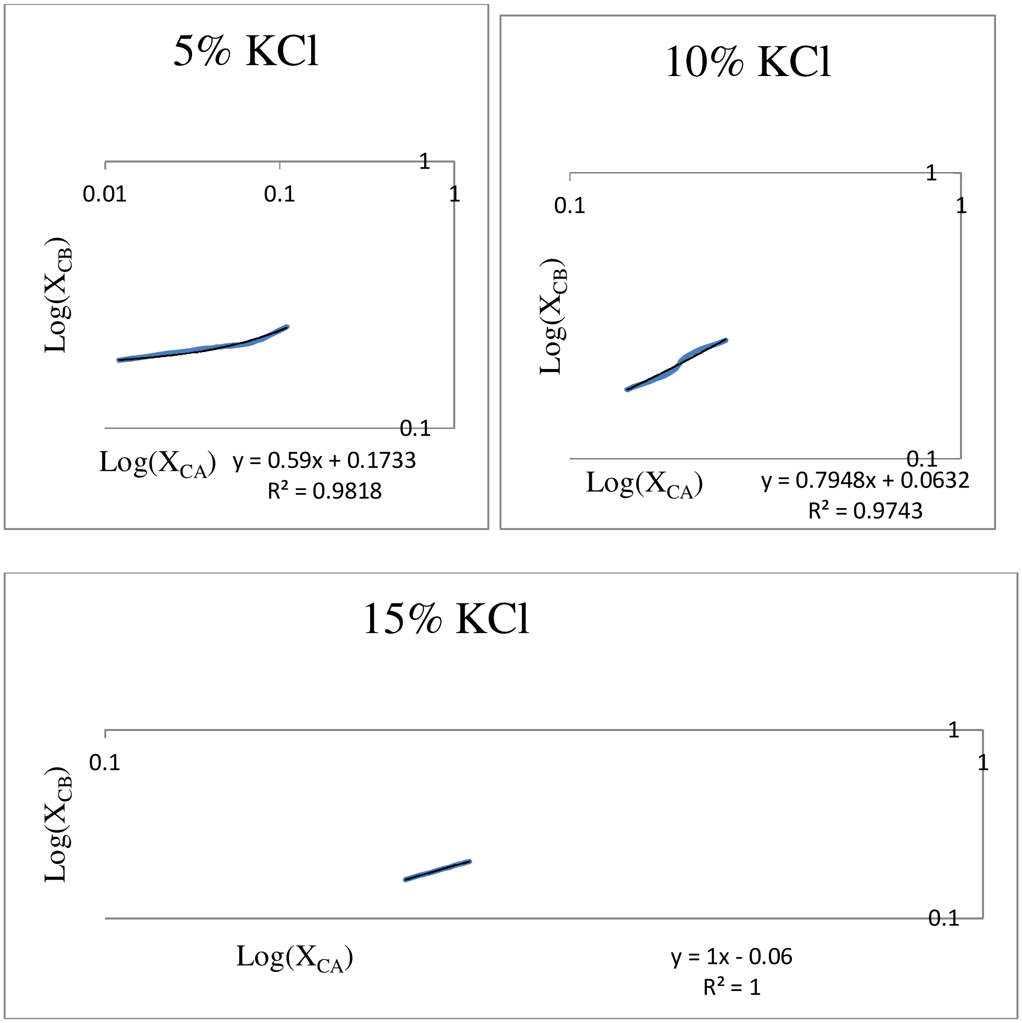

Fig. 36 Determination of Log A & B for KCl (Campbell Equation)

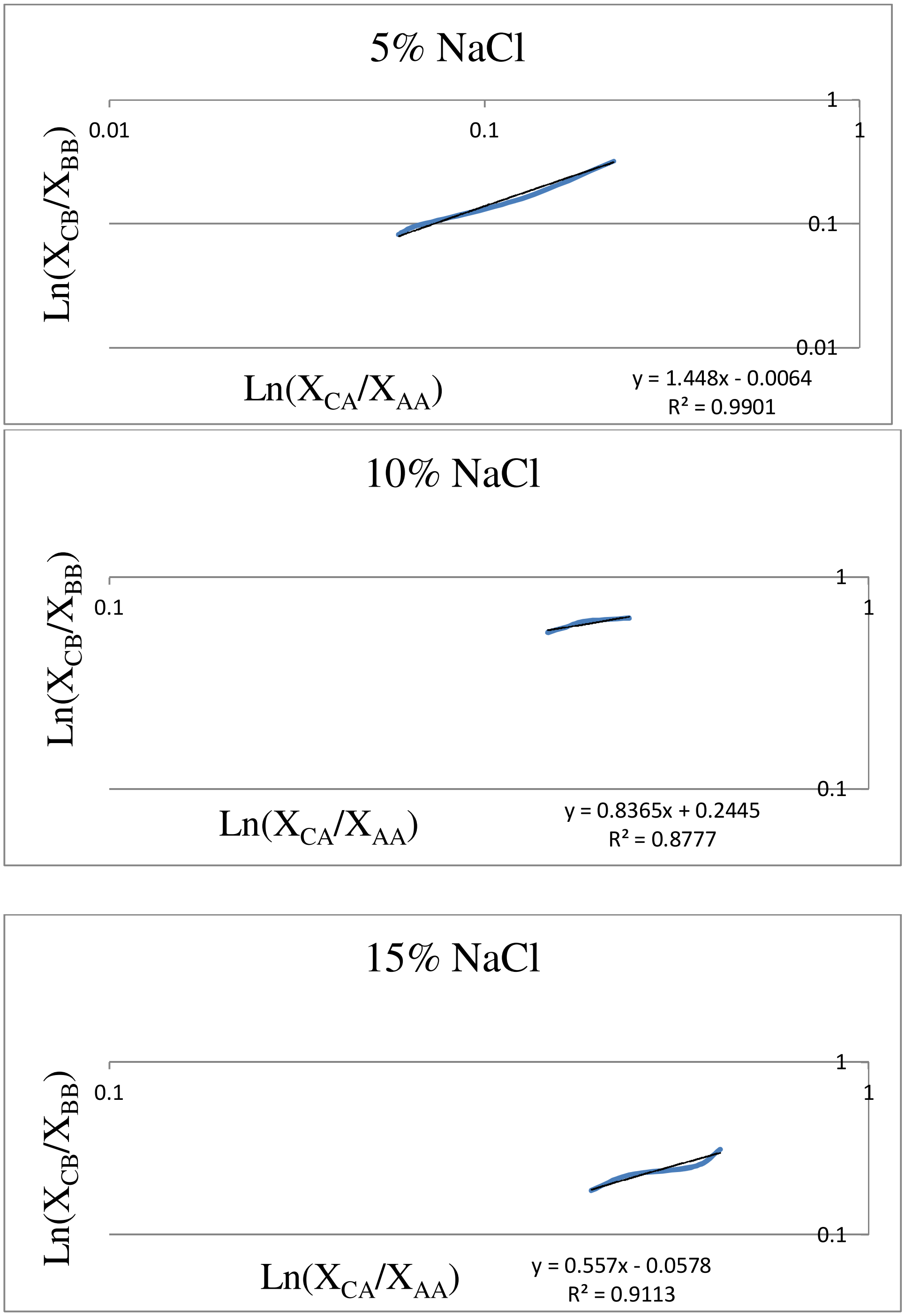

Fig. 37 Determination of Log A & B for NaCl(Hand's Equation)

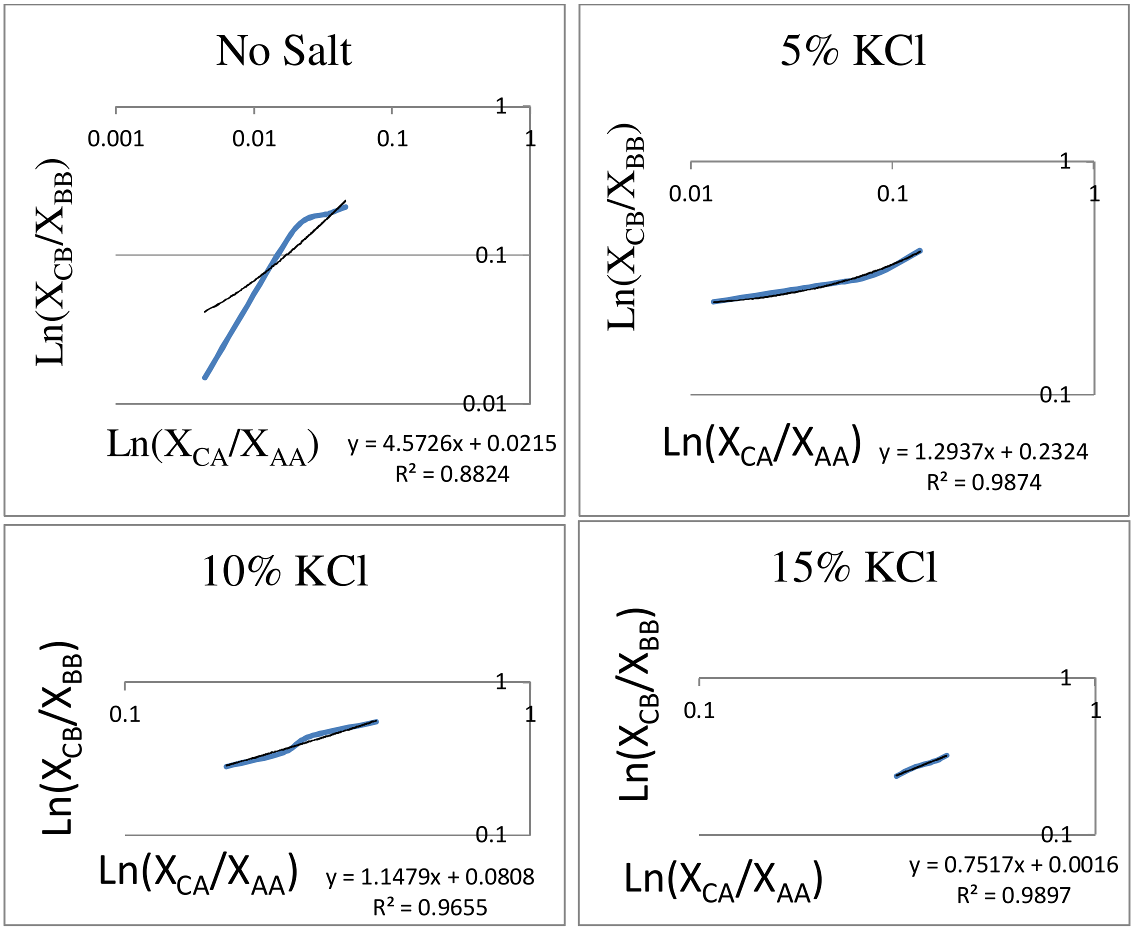

Fig. 38 Determination of Log A & B for KCl(Hand's Equation)

TABLE – 4.1

SOLUBILITY DATA
(For All Systems)

System: Water + Acetone + 1-Butanol

Table 4.1.1

1. NO SALT

SL.No	X_A	X_B	X_C	Refractive Index
1	92.53	7.65	0	1.341
2	80.67	11.62	18.71	1.348
3	65.84	21.33	12.83	1.354
4	52.08	32.25	15.67	1.365
5	44.52	39.34	16.14	1.369
6	39.67	44.09	16.24	1.372
7	37.71	49.63	12.66	1.373
8	33.92	54.33	11.75	1.374
9	30.64	58.98	10.38	1.375
10	25.69	64.0	10.31	1.376
11	21.38	73.56	5.06	1.377
12	19.53	79.82	0.65	1.379
13	16.47	83.21	0.32	1.382

Table 4.1.2 (i)

2. SALT: SODIUM CHLORIDE (NaCl)

(i) 5% By Weight

SL. No	X_A	X_B	X_C	Refractive Index
1	93.65	6.65	0	1.343
2	85.24	10.83	4.03	1.350
3	69.01	21.3	9.69	1.360
4	53.56	30.99	15.45	1.366
5	44.35	37.63	18.02	1.368
6	40.19	41.33	18.48	1.370
7	35.85	44.93	19.22	1.371
8	30.35	50.82	18.83	1.372
9	28.88	54.98	16.14	1.373
10	21.0	63.33	15.67	1.374
11	15.33	72.55	12.12	1.376
12	9.94	82.86	7.20	1.386
13	8.45	88.25	3.3	1.389

Table 4.1.2 (ii)

(ii) 10% By Weight

SL.No	X_A	X_B	X_C	Refractive Index
1	94.9	5.10	0	1.343
2	67.82	5.26	26.91	1.351
3	58.49	10.14	31.37	1.357
4	33.02	34.63	32.35	1.363
5	26.99	39.76	33.24	1.372
6	24.7	45.46	29.85	1.376
7	23.95	56.44	19.61	1.380
8	21.84	65.3	12.86	1.382
9	20.44	69.56	10.0	1.383

Table 4.1.2 (iii)

(iii) 15% By Weight

SL. No	X_A	X_B	X_C	Refractive Index
1	96.7	3.3	0	1.339
2	66.04	7.75	26.21	1.342
3	54.2	15.27	30.53	1.349
4	44.0	23.0	33.0	1.353
5	26.16	36.86	36.98	1.361
6	28.91	51.0	20.18	1.374
7	25.03	56.41	18.56	1.379
8	21.76	65.15	13.08	1.381
9	12.39	82.92	4.68	1.386

Table 4.1.3 (i)

3. SALT: POTASSIUM CHLORIDE (KCl)

(i) 5% By Weight

SL. No	X_A	X_B	X_C	Refractive Index
1	96.3	3.7	0	1.344
2	80.14	10.95	8.91	1.354
3	57.48	21.75	20.77	1.363
4	43.42	32.07	24.51	1.368
5	30.35	46.82	22.83	1.373
6	25.35	48.89	25.75	1.375
7	20.54	50.71	28.74	1.381
8	17.75	58.20	24.04	1.387
9	10.33	75.69	13.98	1.389

Table 4.1.3 (ii)

(ii) 10% By Weight

SL. No	X_A	X_B	X_C	Refractive Index
1	96.45	3.55	0	1.344
2	71.12	8.73	20.15	1.352
3	56.69	16.69	26.62	1.359
4	44.39	24.51	31.1	1.365
5	28.16	41.48	30.36	1.374
6	26.08	48.01	25.91	1.378
7	24.46	57.63	17.91	1.380
8	20.40	63.85	15.75	1.381
9	10.64	74.45	14.9	1.384

Table 4.1.3 (iii)

(iii) 15% By Weight

SL. No	X_A	X_B	X_C	Refractive Index
1	96.6	3.4	0	1.338
2	67.74	7.95	24.31	1.343
3	55.57	15.65	28.78	1.350
4	45.03	23.78	31.19	1.356
5	26.92	37.93	35.15	1.364
6	29.10	51.24	19.66	1.371
7	25.30	57.0	17.7	1.378
8	13.93	73.79	12.28	1.382
9	12.61	84.36	3.03	1.388

TABLE – 4.2

EQUILIBRIUM DATA

(For All Systems)

System: Water + Acetone + 1-Butanol

TABLE -4.2.1

1. NO SALT

Water Layer				
SL. No.	X_{AA}	X_{BA}	X_{CA}	Refractive Index
1	0.86	0.11	0.13	1.354
2	0.882	0.099	0.125	1.352
3	0.893	0.089	0.108	1.347
4	0.915	0.081	0.09	1.342

Butanol Layer				
SL. No.	X_{AB}	X_{BB}	X_{CB}	Refractive Index
1	0.305	0.588	0.124	1.3728
2	0.272	0.61	0.116	1.374
3	0.261	0.632	0.096	1.376
4	0.198	0.775	0.012	1.379

TABLE -4.2.2(i)

2. SODIUM CHLORIDE (NaCl)

(i) 5% By weight

Water Layer					
SL. No.	X_{AA}	X_{BA}	X_{CA}	%Wt. Salt	Refractive index
1	0.588	0.275	0.13	3.21	1.363
2	0.709	0.187	0.09	3.92	1.358
3	0.827	0.125	0.055	4.08	1.354
4	0.851	0.1083	0.051	4.5	1.352

Butanol Layer					
SL. No.	X_{AB}	X_{BB}	X_{CB}	%Wt. Salt	Refractive Index
1	0.261	0.566	0.18	1.69	1.372
2	0.143	0.75	0.12	1.22	1.377
3	0.11	0.827	0.08	0.61	1.382
4	0.099	0.849	0.07	0.60	1.384

TABLE -4.2.2(ii)

(ii) 10% By weight

Water Layer					
SL. No.	X_{AA}	X_{BA}	X_{CA}	%Wt. Salt	Refractive index
1	0.61	0.088	0.295	5.94	1.356
2	0.663	0.05	0.28	6.33	1.352
3	0.676	0.077	0.27	7.56	1.349
4	0.687	0.053	0.26	8.2	1.348

Butanol Layer					
SL. No.	X_{AB}	X_{BB}	X_{CB}	%Wt. Salt	Refractive Index
1	0.244	0.468	0.3	4.19	1.376
2	0.24	0.47	0.29	3.62	1.3764
3	0.239	0.481	0.28	2.31	1.377
4	0.22	0.492	0.27	1.8	1.3774

TABLE -4.2.2(iii)

(iii) 15% By weight

Water Layer					
SL. No.	X_{AA}	X_{BA}	X_{CA}	%Wt. Salt	Refractive index
1	0.525	0.158	0.335	9.21	1.354
2	0.533	0.153	0.314	11.02	1.350
3	0.599	0.111	0.29	11.54	1.346
4	0.6265	0.1035	0.27	13.4	1.343

Butanol Layer					
SL. No.	X_{AB}	X_{BB}	X_{CB}	%Wt. Salt	Refractive Index
1	0.18	0.625	0.195	5.79	1.376
2	0.17	0.665	0.165	4.0	1.378
3	0.168	0.675	0.15	3.26	1.380
4	0.163	0.698	0.13	1.25	1.382

TABLE -4.2.3 (i)

3. SALT: POTASSIUM CHLORIDE (KCL)

(i) 5% By weight

Water Layer					
SL. No.	X_{AA}	X_{BA}	X_{CA}	%Wt. Salt	Refractive index
1	0.80	0.09	0.11	3.15	1.366
2	0.8625	0.0625	0.07	3.3	1.362
3	0.9125	0.05	0.04	3.5	1.356
4	0.915	0.041	0.012	4.32	1.348

Butanol Layer					
SL. No.	X_{AB}	X_{BB}	X_{CB}	%Wt. Salt	Refractive Index
1	0.183	0.577	0.24	1.55	1.387
2	0.147	0.643	0.21	1.68	1.3875
3	0.124	0.676	0.20	1.46	1.3876
4	0.122	0.698	0.18	0.77	1.388

TABLE -4.2.3 (ii)

(ii) 10% By weight

Water Layer					
SL. No.	X_{AA}	X_{BA}	X_{CA}	%Wt. Salt	Refractive index
1	0.599	0.151	0.25	6.13	1.359
2	0.698	0.102	0.20	7.3	1.352
3	0.731	0.089	0.18	7.37	1.349
4	0.783	0.077	0.14	8.34	1.346

Butanol Layer					
SL. No.	X_{AB}	X_{BB}	X_{CB}	%Wt. Salt	Refractive Index
1	0.27	0.47	0.26	3.95	1.377
2	0.248	0.522	0.23	2.80	1.3772
3	0.223	0.577	0.20	2.48	1.378
4	0.215	0.61	0.175	1.11	1.380

TABLE -4.2.3 (iii)

(iii) 15% By weight

Water Layer					
SL. No.	X_{AA}	X_{BA}	X_{CA}	%Wt. Salt	Refractive index
1	0.615	0.125	0.26	10.1	1.346
2	0.632	0.118	0.25	11.45	1.344
3	0.676	0.089	0.235	12.63	1.342
4	0.698	0.082	0.22	12.87	1.340

Butanol Layer					
SL. No.	X_{AB}	X_{BB}	X_{CB}	%Wt. Salt	Refractive Index
1	0.175	0.625	0.20	4.7	1.372
2	0.167	0.643	0.19	3.53	1.374
3	0.162	0.654	0.175	2.27	1.376
4	0.158	0.676	0.16	2.26	1.378

TABLE – 4.3

1. COSTANTS Ln A AND B IN MODIFIED CAMPBELL EQUATION

Table 4.3.1

SALT	% Wt.	Ln A	B
NO SALT	0	0.0165	3.0335
NaCl	5	0.0021	1.3544
	10	0.0475	0.8598
	15	-0.1289	0.956
KCl	5	0.1733	0.59
	10	0.0632	0.7948
	15	-0.06	1.0

2. COSTANTS Ln A AND B IN HAND'S Plot

Table 4.3.2

SALT	% Wt.	Ln A	B
NO SALT	0	0.0215	4.5726
NaCl	5	-0.0064	1.44
	10	0.2445	0.8365
	15	-0.0578	0.557
KCl	5	0.2324	1.2937
	10	0.0808	1.1479
	15	0.0016	0.7517

TABLE-4.4

1. CONSTANTS a, b, c, d IN MODIFIED CAMPBELL EQUATION

Table – 4.4.1

SALT	% Wt.	a	b	c	d	Regration Co-efficient
NO SALT	0	0.0165		3.0335		0.8588
NaCl	5	0.0165	-0.0028	3.0335	-0.335	0.9957
	10	0.0165	0.0031	3.0335	-0.217	0.9888
	15	0.0165	-0.0096	3.0335	-0.1358	0.9751
KCl	5	0.0165	0.0314	3.0335	-0.4887	0.9818
	10	0.0165	0.00467	3.0335	-0.2238	0.9743
	15	0.0165	-0.0051	3.0335	-0.1355	1

2. CONSTANTS a, b, c, d IN EISEN-JOFFE EQUATION

SALT	% Wt.	a	b	c	d	Regration Co-efficient
NO SALT	0	0.0215		4.5726		0.8824
NaCl	5	0.0215	-0.0055	4.5726	-0.6265	0.9901
	10	0.0215	0.0223	4.5726	-0.3736	0.8777
	15	0.0215	-0.0053	4.5726	-0.2677	0.9113
KCl	5	0.0215	0.0422	4.5726	-0.6557	0.9874
	10	0.0215	0.0059	4.5726	-0.3425	0.9655
	15	0.0215	-0.0013	4.5726	-0.255	0.9897

TABLE – 4.5

COMPARISION BETWEEN X_{CB} – OBSERVED AND X_{CB} CALCULATED

Table 4.5.1

1. SALT : SODIUM CHLORIDE (NaCl)

% Wt. Salt		Campbell Equation		Eisen-Joffe Equation	
	X_{CB} observed	X_{CB} Calculated	% Error	X_{CB} Calculated	% Error
5	0.18	0.063	65	0.0634	64.77
	0.12	0.0385	67.9	0.0374	68.83
	0.08	0.0197	75.4	0.0162	79.75
	0.07	0.0178	74.5	0.0142	79.71
10	0.3	0.391	30.3	0.447	49.0
	0.29	0.373	28.62	0.401	38.27
	0.28	0.362	29.3	0.391	39.64
	0.27	0.350	29.63	0.383	41.85
15	0.195	0.261	33.85	0.0426	78.15
	0.165	0.245	48.48	0.0433	73.75
	0.15	0.227	51.33	0.0394	73.73
	0.13	0.212	63.07	0.382	70.61
Standard Deviation-0.1385				Standard Deviation0.1806	
Root Mean Square Deviation-0.0808				Root Mean Square Deviation-0.1292	

Table 4.5.2

2. POTASSIUM CHLORIDE (KCl)

% Wt. Salt		Campbell Equation		Eisen-Joffe Equation	
	X_{CB} observed	X_{CB} Calculated	% Error	X_{CB} Calculated	% Error
5	0.24	0.405	68.75	0.0756	68.5
	0.21	0.310	47.61	0.049	76.66
	0.20	0.223	11.5	0.0203	89.85
	0.18	0.109	39.44	0.0433	75.94
10	0.26	0.384	47.69	0.207	20.38
	0.23	0.322	40.0	0.149	35.21
	0.20	0.295	47.5	0.138	31.0
	0.175	0.242	38.28	0.101	42.28
15	0.20	0.226	13.0	0.327	63.5
	0.19	0.217	14.21	0.321	68.94
	0.175	0.204	16.57	0.296	69.14
	0.16	0.192	20.0	0.285	78.13
Standard Deviation-0.0813				Standard Deviation-0.1103	
Root Mean Square Deviation-0.0834				Root Mean Square Deviation-0.1245	

RESULT AND DISCUSSION

The liquid-liquid equilibrium for the given ternary system was observed at atmospheric pressure and a temperature of 25^0C. The ternary solubility data and the tie line data are determined in the presence of NaCl, KCl at 5%, 10% and 15% concentration for the system water + acetone + 1-butanol at same temperature. It had seen from the diagram that the addition of salts accelerate the distribution in favour of 1-butanol layer especially at higher salt concentration. The solubility decreases in presence of the salt and increases the heterogeneous zone of the system. Heterogeneous area plays an important role in liquid-liquid equilibrium. In the supplied system, it was seen that the areas of the solubility curve are more in case of salt addition than that of without salt. More acetone is shifted towards the butanol phase with increasing salt concentrations. This process is generally known as “salting out effect” and is caused by the fact that the presence of high amount of hydrated ions decreases the availability of the water molecules in the aqueous phase to the salvation of other solvents. The concentration of acetone in organic phase increases by presence of salts and hence enlargement of the two phase region occurred. These process increase with salt concentration and are maximum at salt saturation. From the binodial curve it is seen that the salting out effect is more in NaCl. Hence the order of effectiveness of salt was as follows.

NaCl > KCl. The orders of effectiveness of the salts based on the salt effect parameter were derived from Eisen – Joffee Equation and modified Campbell equation.

CHAPTER – 5

CONCLUSION

The liquid-liquid equilibrium diagram for ternary system water + 1-butanol + acetone was determined at 25^0C. The effects of salt like NaCl and KCl on the ternary system at different concentrations were observed at the same temperature. Eisen – Joffe and Campbell correlations are used for the determination of the corresponding parameters for the given system with and without salt, which are appropriate for interpolation of the equilibrium data. In case of all the systems containing dissolved salt, under study it is observed that at lower concentration modified Campbell equation gives more error. From the present experiment it was seen that modified Campbell equation correlate better in presence of NaCl compared to KCl. The experimental results lead to the conclusion that a salting out effect exists for all the salts under study, increasing for higher salt concentrations. In conclusion it may be indicated that concerted efforts on the observations of the salt effect on the distribution of a solute between two partially miscible liquids have a potential scope for engineering applications.

The use of solid inorganic salt in place of liquid separating agent in extraction process has great advantages. It is because by use of small amount of solid salt bring about a substantial change in phase equilibrium in ternary liquid system. This fact is observed and conformed in case of ternary system under investigation. Thus it is concluded that this technique can be used effectively for extraction of liquid (solute) using solid salt.

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