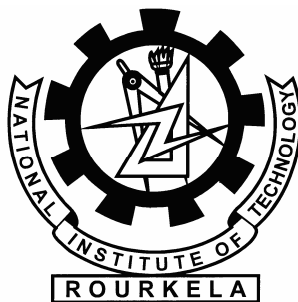A
Project Report on

SALT EFFECT ON LIQUID LIQUID EQUILIBRIUM
FOR TERNARY SYSTEM
WATER +1-PROPANOL +ETHYL ACETATE

In partial fulfillment of the requirements of

Bachelor of Technology (Chemical Engineering)

Submitted By

Mahendra Kumar Khuntia (Roll No.10400042D)
Jyoti Ranjan Swain (Roll No.10300043)
Session: 2006-07

Department of Chemical Engineering
National Institute of Technology
Rourkela-769008
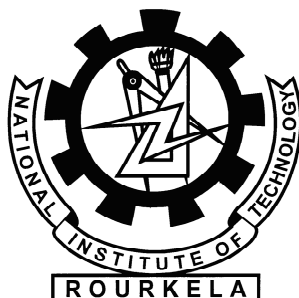**Orissa**

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Under the Guidance of

Dr. Pradip Rath

Department of Chemical Engineering
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National Institute of Technology
Rourkela

CERTIFICATE

This is to certify that that the work in this thesis report entitled "salt effect on liquid liqu

equilibrium for ternary system water +1-propanol +ethyl acetate" submitted by Mahend

Kumar Khuntia and Jyoti Ranjan Swain in partial fulfillment of the requirements for tl

degree of Bachelor of Technology in Chemical Engineering Session 2003-2007 in tl

department of Chemical Engineering, National Institute of Technology Rourkela, Orissa

an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge the matter embodied in the thesis has not been submitted to

any other University /Institute for the award of any degree.

Date: Prof. (Dr) Pradip Rath
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Chemical Engineering

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CONTENTS

ABSTRACT:-

Liquid/liquid extraction is a very common method used in the organic laboratory. Organic reactions often yield a number of by-products, some inorganic, some organic... Liquid/liquid extraction is often used as the initial step in the work-up of a reaction, before final purification of the product by recrystallization, distillation or sublimation.

Salting-out effect can be used to improve the extraction of some solutes by modifying the solute distribution between two liquid phases. Experiments are conducted on the system Water + 1-propanol + Ethyl acetate with varying salt concentrations and varying temperatures. The basic objective of this project is to determine the best temperature range and the salt from NaCl and $(NH_4)_2SO_4$ which enhances the separation or extraction of the solute by the specified solvent. The experiments were conducted and the resulting extract and raffinate phase was analyzed with the help of the gas chromatography. The plots of voltage vs time was obtained from the gas chromatography, showing the percent volume of the different components present in both the phases. For each phase a separate plot is obtained.

Here we have considered two salts: NaCl and $(NH_4)_2SO_4$. We have tried to show the effect of these two salts on the system at temperatures 27ºC, 32ºC and 37ºC.The solubility data are tabulated in Table 5.1 and the equilibrium data are tabulated in Table 5.2. Considering these data the solubility curves and the distribution curves were plotted. All salt containing data are reported on salt free basis. The experimental tie-line data under no salt condition were determined and presented in respective tables. It can be seen from the diagrams that the addition of the salts shifts the distribution in favour of ethyl acetate layer especially at higher salt concentrations. The presence of the salt decreases the solubility of the system increasing the heterogeneous zone. Heterogeneous area is an important characteristic. In the present system, the areas of the solubility curves are more in case of salt addition than that of without salt. At increasing salt concentrations more 1-propanol is transferred to the ethyl acetate phase. This process is usually referred to as salting out and is caused by the fact that the presence of high amounts of hydrated ions reduces the availability of the water molecules in the aqueous phase to the salvation of other solvents. Presence of salts mainly increase the concentrations of 1-propanol in organic phase and hence enlargement of the two-phase region occurred.

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CHAPTER-1

INTRODUCTION

1. INTRODUCTION

Separation processes in which two immiscible or partially soluble liquid phases are brought into contact for the transfer of one or more components are referred to as liquid-liquid extraction or solvent extraction. The processes taking place are primarily physical, since the solutes being transferred are ordinarily recovered without chemical change. On the other hand the physical equilibrium relationships on which such operations are based depends mainly on the chemical characteristics of the solutes and solvents. Thus, use of a solvent that chemically resembles one component of a mixture more than the other components will lead to concentration of that component in the solvent phase, with the exclusion from that phase of dissimilar components.

Liquid-liquid extraction process is based on the transfer of a dissolved component from its solvent to a second solvent in order to bring about any one of several effects. The second solvent has to be immiscible with the first solvent and preferably has a higher affinity to the transferred component. Liquid-liquid extraction can purify a component with respect to dissolved components that are not soluble in the solvent. The solute distributes between both diluents and solvent until liquid-liquid equilibrium is reached. Since diluents and solvent are immiscible the two phases can be separated and the process can be repeated at different condition.

An accurate thermodynamic model is required to calculate the liquid-liquid equilibria and the distribution of the solute between the liquid phases. Many thermodynamic models are available that is able to give an accurate description of distribution of product between two liquid phase. 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 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 a solutropic solution. By adding a suitable salt the tie lines of a liquid-liquid equilibrium mixture can be significantly changed, even to the extent of eliminating the solutrope.

1.1 IMPORTANCE AND APPLICATION

Liquid-liquid extraction is an easy method which is generally preferred over other methods. Some of the reasons why liquid-liquid extraction is preferred are as follows:-

➢ When separation by distillation is ineffective or very difficult, liquid-liquid extraction is one of the main alternatives to consider. Close boiling mixtures or substances that cannot withstand the temperature of distillation, even under a vacuum, may often be separated from impurities by extraction, which utilizes chemical differences instead of vapour-pressure differences.

➢ It is like a substitute for the chemical methods. Since chemical methods consume reagents and frequently lead to expensive disposal problems for chemical byproducts. But liquid extraction has less chemical consumption and also less byproduct formation. Here in this case also the solvent recovered is utilized as the reflux .Thus this process is less costly in comparison with the other methods.

➢ In comparison with other methods it is less costly .Other separation methods like distillation and evaporation heat or steam is required which increases the cost .but liquid-liquid extraction is the simple extraction methods using chemicals, thus it is relatively less costly. Metal separations such as uranium-vanadium, hafnium-zirconium, and tungsten-molybdenum are more economical by liquid-liquid extraction.

Simple extraction process is a time consuming and a low effectiveness. So salt is added to increase the effectiveness of separation and less time is required. The addition of an electrolyte to a solvent mixture modifies the interaction among the various solvent and solute molecules resulting in shifting their phase equilibrium.

The addition of an electrolyte to a solvent mixture modifies 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. The simulation and design

of industrial extraction process involving electrolytes depends heavily on the availability of models that can be described in influence of ion on the phase behaviors. The presence of charge species in a mixed solvent solution appreciably influence of the charge distribution of solute between the liquid phases.

These types of extraction using salt are used in industrial processes. Some examples are as follows:-

➢ Extraction of caprolactum from benzene using nylon-6.

➢ Presence of ammonium sulfate in newer production processes of caprolactum.

➢ Determination of alcohol in wine using sodium chloride salt.

➢ Tantalum and niobium can be separated by liquid extraction of the hydrofluoric acid solutions with methyl isobutyl ketone.

1.2 LIQUID-LIQUID EXTRACTION

Extraction is the drawing or pulling out of something from something else. Liquid-liquid extraction is the separation of the constituents of a liquid solution by contact with another insoluble liquid. It is also called as solvent extraction. If the substances constituting the original solution distribute themselves differently between the two liquid phases, a certain degree of separation will result and this can be enhanced by use of multiple contacts or their equivalent in the manner of gas absorption and distillation.

Liquid/liquid extraction is a very common method used in the organic laboratory. An organic reaction often yields a number of by-products, some inorganic, some organic... Liquid/liquid extraction is often used as the initial step in the work-up of a reaction, before final purification of the product by recrystallization, distillation or sublimation. A simple example will indicate the scope of the operation and some of its characteristics. If a solution of acetic acid in water is agitated with a liquid such as ethyl acetate, some of the acid but relatively little water will enter the ester phase. Since at equilibrium the densities of the aqueous and ester layers are different, they will settle when agitation stops and can be decanted from each other. Since now the ratio of acid to water in the ester layer is different from that in the original solution and also

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different from that in the residual water solution, a certain degree of separation will have occurred. This is an example of stage wise contact, and it can be carried out either in batch or in continuous fashion. The residual water can be repeatedly extracted with more ester to reduce the acid content still further, or we can arrange a countercurrent cascade of stages. Another possibility is to use some sort of countercurrent continuous-contact device, where discrete stages are not involved. The use of reflux, as in distillation, may enhance the ultimate separation still further.

In all such operations, the solution which is to be extracted is called the feed, and the liquid with which the feed is contacted is the solvent. The solvent-rich product of the operation is called the extract, and the residual liquid from which solute has been removed is called as the raffinate.

Extraction involves the use of systems composed of at least three substances, and although for the most part the insoluble phases are chemically very different, generally all three components appear at least to some extent in both phases. Thus liquid-liquid extraction is generally represented by the tie-lines and the equilateral-triangular coordinates. These are used extensively in the chemical literature to describe graphically the concentrations in ternary systems. Triangular diagrams are used for representing three-component systems. Every possible composition of the ternary mixture corresponds to a point in the diagram.

It is the property of an equilateral triangle that the sum of the perpendicular distances from any point with in the triangle to the three sides equals the altitude of the triangle. Therefore the altitude represents 100 percent composition and the distances to the three sides the percentages or the fractions of the three components. 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 these triangular diagrams the left vertex generally represents the diluents, right vertex as the solvent and the top as the solute. The sides of the triangle represent the corresponding two-component system.

The mass fraction of each component is given by lines parallel to the side opposite to the corner which represents the pure component. The numbering can be placed at edges of the triangle in which case it is advisable to extend the lines. The numbers can also be inserted in the middle of the lines, this makes the diagram easier to use. Thus the plotting of the values for the percentages of any two compounds of a ternary system determines a point in the triangle, fixes the percentages of the third component, and checks the corresponding mass fractions of all the

three components. As every point in a triangular diagram corresponds to a composition there is no coordinate free for another reference variable.

If the ternary system exists in two phases, then the 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 extractions, and the boundary lines between the liquid single-phase region and the two phase regions particularly important. This boundary line is called as the bimodal curve. Every point in the binodial curve is in equilibrium with another binodial point. The interaction of the diluent and solvent branches of the curve is called the plait point and has some unique characteristics. It represents simultaneously a solvent and a diluent phase, and is a point where both phases have the same composition and density. The line which connects points in equilibrium with one another is called as the tie lines. All mixture, which corresponds to a point on a tie line separate into two phases. The composition of these phases is given by the end points of the tie lines and their quantities are given by lever rule. The equilibrium data have to be determined experimentally in each individual case.

1.3 SALT EFFECT ON LIQUID-LIQUID EXTRACTION

The addition of a salt to an aqueous solution of a volatile non electrolyte has a marked effect upon the liquid-liquid and vapour-liquid equilibria of the solution. The presence of the salt may either raise or lower the relative volatility of the nonelectrolyte or in extreme cases cause the formation of the two liquid phases. The observed effects depend upon the nature and concentration of both the salt and nonelectrolyte. Generally salt has a considerable effect on the solvent to which it is added. It changes the general properties or characteristics of the solvent. As soon as any salt dissolves in the water, the boiling point of the water gets affected when salt is added are as follows:-

➢ Lowering of the vapour pressure
➢ Elevation in boiling point
➢ Depression in freezing point
➢ Change in osmotic pressure

The addition of non-volatile solute to a solvent mixture modifies the interaction among the various solvent solute molecules resulting in shifting their phase equilibrium even to the extent of eliminating the solutrope in liquid-liquid equilibrium. 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 the organic solvent component resulting in considerable reduction of the energy cost incurred in the recovery and purification of the organic solvent. The distribution of the solute between the two liquid phases mainly depends upon the concentration of electrolyte. The electrolyte will remain in the phase in which it is most soluble and other solute will be transferred to the phase that 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. When salt is added to the liquid components the structure of the liquid components may be altered by promoting, destroying or otherwise affecting interaction between the liquid components, there by altering the selectivity properties of one of the liquid component. The result is then a solvent is added to extract a solute from a liquid mixture in which a salt is dissolved, the distribution of solute between the two solvents gets altered. This may be due to the preferential association of the solute molecules with any one of the solvents in which the salt is dissolved. Thus the separation becomes easier in presence of the salt.

Addition of the salt to an aqueous solution of the ternary system increases the heterogeneity significantly. The area of heterogeneity is more as compared to no salt condition. It also enhances distribution coefficients and selectivity's. Salt mainly affects the mutual solubility of solute and water and the distribution coefficient of solute. The selectivity, which is a ratio of distribution coefficient of solute to that of water, is changed much more by the salt addition than is the distribution coefficient of the solute alone.

CHAPTER-2

THEORIES OF SALT EFFECT

AND

THERMODYNAMIC MODELS

2.1 THEORIES OF SALT EFFECT

Generally the salt effects on the phase equilibrium can be explained by different theories proposed by the well known individuals. The presence of a salt or a non-volatile solute in a solvent mixture can significantly change its equilibrium composition. The salt effect theories are generally concerned with the calculations of ion-electrolyte interaction parameters, which is known as the "salting-out parameter", and the later is used to indicate the magnitude of the salt effect. Positive values indicate the salting out and the negative value indicates the salting in effect. The causes and effect of polar attraction of a dissolved salt for one component of a water non-electrolyte solution have been explained by various theories. These theories can be explained with respect to hydration, electrostatic interaction, internal pressure and vanderwaals forces.

> ## 2.1.1 HYDRATION THEORY

According to this theory each salt ion binds a constant number of water molecules as a shell of oriented water dipoles surrounding the ion, there by decreasing the activity of the water. This bound water is then unavailable as solvent for the nonelectrolyte. The number of water molecules so bound by each salt ion is called the hydration number of the ion. Considering the wide variation in hydration numbers this concept permits only a qualitative estimate of the magnitude of the salt effect. This theory also doesn't allow the occurrence of salting in effect. This theory explains the differences in effects due to solutes and ions by assuming that each ion orients water molecules in a definite direction. If the orientation is favorable to the non-electrolyte molecules, salting-in occurs whereas an unfavorable orientation produces salting-out.

Addition of a salt to liquid-liquid equilibrium introduces ionic forces that affect the equilibrium. When the ions are solvated, part of the water molecules become unavailable for the solutions and they are salted out from the aqueous phase. This salt effect can be used for removing organic compounds from water. In other hand when a polar solvent is added to an aqueous salt solution, it captures the water molecules that were solvated the ions in a salting in affect. This effect may be used for recovering salt from concentrated aqueous solutions.

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> ## 2.1.2 ELECTROSTATIC THEORY

This theory was proposed by Meranda and Furter in 1974 but later it was developed by Debye and Mc Auley. It was based on the amount of work necessary to discharge the ions in the solvent and to recharge them in a solution containing non-electrolyte. This quantity yields the electrostatic contribution to the chemical potential of the neutral solute. The theory thus takes into account only electrostatic effects. It does not allow for the influence of dispersion type forces between the ion and the solute molecules or for the alteration which the ion may produce in the hydrogen bond interactions between neighboring water molecules.

This theory says that the addition of relatively small amount of salt may exerts large effects on the relative volatility of components. The salt dissolved in a mixed solvent may affect the boiling point, the mutual solubility's of the two liquid components. Generally the particles (non-dissociated molecules or ions or both) of dissolved salts tend to attract preferentially one type of solvent molecules more strongly than the other. Usually the molecules of the more polar components are preferentially attracted by the electrostatic field of the ions and hence the vapour composition is enriched by the less polar solvent, in which the salt is less soluble. Kirk wood taking into account the repulsion between the ionic charges and an image charge induced in the cavity created in the solvent by the electrolyte molecule calculated the ion non-electrolyte interaction energy. He derived an equation quite similar in form to that of Debye and Mc Auley.

The electrostatic theory basically considers only the action of columbic forces and omits other factors. Because of simplification and approximations made in its derivation, the Debye-Mc Auley equation is a limiting equation only. Butler, using a similarly simplified model, obtained an equation virtually identical with that of Mc Auley. Later Debye, taking into account the heterogeneity of the mixture of water and neutral solute, expressed the total free energy of the system, including the contribution due to the field of ion, as a function of distance from the ion .These electrostatic theories treats the solvent as a structural continuum, through which the electrostatic ions are determined solely by their macroscopic electric constants.

➢ 2.1.3 VANDERWAALS FORCES THEORY

A given non-electrolyte may be salted-in by some electrolyte and salted-out by other in same solvent. This fact suggested that short range dispersion forces might also be applicable in determining salt effect especially at finite concentration. Long and Mc.Davit in an attempt to allow for the trends towards salting-in of the non-electrolyte by large ions, proposed a modified version of the Kirkwood and Debye equation to account for dispersion and displacement of forces. They concluded that this theory was included in establishing the note of dispersion forces.

Since the electrostatic interaction between an ion and a neutral molecule is short range in nature, additional interaction or Vander Waals type must be considered more fully. These terms involves the polarizability of salt ions, solvent molecules, and non-electrolyte solute molecules, as higher selectivity in extraction system with salt. The lower distribution coefficient of water can be means a good attributed to the association of water molecules in unrestricted salt in the aqueous phase, which impedes a transfer of water to the organic phase. From practical point of view resulting higher selectivity well as the special force fields originating from any component dipoles that may be present.

Bergen and Long disused salting-in and salting-out in terms of the effectiveness of the electrolyte on the degree of order in the solvent structure. Gross indicated that salting-in indicate a preferential attraction of ion for the non-electrolyte over the solvent. In the presence of the large ions having weak electrostatic fields or in the presence of relatively un-dissociated salt, the highly polar water molecule may tend to associate much more strongly with each other than with the solvent forcing the salt into the vicinity of the less polar non-electrolyte molecules with which the salt is associated.

➢ 2.1.4 INTERNAL PRESSURE THEORY

According to the internal pressure concept proposed by Tammann and applied by Mc. Davit and Long, the concentration in total volume upon the addition of salt to water can be thought of as a compression of the solvent. This compression makes the introduction of a

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molecule of non-electrolyte more difficult, and this result in salting out. An increase in total volume upon the addition of a salt would produce the counter effect known as salting in. Mc. Davit and Long, applying the internal pressure concept of Tammann to nonpolar non-electrolytes, calculated the free energy of the transfer of the latter from pure water to the salt solution.

2.2 SALTING-IN AND SALTING-OUT EFFECT

The presence of a salt or a non-volatile solute in a solvent mixture can significantly change its equilibrium composition. Addition of a salt to liquid-liquid equilibrium introduces ionic forces that affect the equilibrium. If an electrolyte is added to water, it is usually found that the solubility of a non-electrolyte in the ionic solution thus formed is lower than in pure water. It means solubility decreases; this is known as salting-out effect. 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 the solution. This salting out effect is not restricted to dilute3 solutions or solutions of non-polar substances. Thus one salt may be salted-out by another and colloidal substances may be salted out. In general, polar substances tend to be salted out rather less readily than on-polar substances.

One explanation which has been brought forward to explain the salting-out depends on the supposition that the water molecules in an ionic solution tend to from compact clusters around the ions. The formation of such cluster is an energetically favorable process, which will be preferred at the expenses of the formation of the rather different cage structures, which are believed to surround a non-electrolytic solute molecule. In other words, the water molecules which surround the ions are not available for the solution of non-electrolytes. The reason given for the greater effectiveness of the smaller ions is that these have a greater charge density for a given volume of ion and that it is this property which dictates the degree of hydration of the ion, and hence it's salting-out power. The rule that the salting-out power of an ion decreases as its size increases is however, only roughly true and there are exceptions, particularly in the cases of the smallest cat ions.

Very large ions produce increased solubility or salting-in. This phenomenon was first studied by Neuberg and was called by him hydrotropism. The phenomenon has been most extensively studied in the case of polar non-electrolyte solutes. The concept of ion hydration, used to explain salting out, does not explain why very large ions should produce an actual enhancement of the solubility. This effect may be due in part to the large dispersion type attractive forces, which will exist between the non-polar part of these ions and the solute molecules. These ion-solute interactions would be expected to increase with the size of the ion and would tend to produce a congregation of non-electrolyte molecules around the ions at the expense of the water molecules. A large ion with an unsymmetrical charge distribution and a prominent non-polar region might be expected to show this effect particularly strongly, and such ions do in fact cause salting-in in many cases.

Another reason why large ions produce salting-in may be that these ions, when dissolved in water distort the water structure in their vicinity and create a fluid in which the degree of hydrogen bonding is less than that of pure water. This would be expected to produce an enhancement of the solubility of the foreign solute molecule. This aspect of salting in has been stressed particularly by Long and McDavit. It is probable that both the above mechanisms are in fact operative. Salting may also occur in cases where a specific chemical reaction takes place between the solute and salt ions.

It has been calculated by previous experimental findings that the magnitude of the salt effect in a given system mainly depends on the concentration of the salt present in the solution which can be expressed in terms of a salt effect parameter. In turn, salt effect parameter is a function of the factors such as degree of differences of solubility of the salt in the solution, ionic charges, ionic radii and others.

2.3 THERMODYNAMIC MODEL

2.3.1 UNIQUAC MODEL (Universal quasi-chemical model)

At liquid-liquid equilibrium, the composition of the two phases (Raffinate phase & extract phase) can be determined from the following equations:

$$(\gamma_i \chi_i)_1 = (\gamma_i \chi_i)_2 \text{------------------- (1)}$$

$$\sum \chi_{i_1} = \sum \chi_{i_2} = 1 \text{------------- (2)}$$

Here γ_{i_1} & γ_{i_2} are the corresponding activity coefficient of component i in phase - 1(Raffinate phase) and phase -2(extract phase).Equation 1 & 2 are solved for the mole fraction(x) of component `i` in the two liquid phases. This method of calculation gives a single tie line. The UNIQUAC model is given by Abrams & Prausnitz.

$$\frac{g^E}{RT} = \sum_{i=1}^{C} X_i Ln\left(\frac{\Phi_i}{X_i}\right) + \frac{Z}{2}\sum_{i=1}^{C} q_i X_i Ln\left(\frac{\Theta_i}{\Phi_i}\right) - \sum_{i=1}^{C} q_i X_i Ln\left(\sum_{j=1}^{C}\Theta_j \tau_{ji}\right) \text{------------- (3)}$$

Or, $\quad Ln\ \gamma_i = Ln\gamma_i^C + Ln\gamma_i^R$ ---------- (4)

Where, $Ln\gamma_i^C = Ln\left(\frac{\Phi_i}{X_i}\right) + \frac{Z}{2}q_i Ln\left(\frac{\Theta_i}{\Phi_i}\right) + \tau_i - \frac{\Phi_i}{X_i}\sum_{j=1}^{C} X_j \tau_j$ ----------- (5)

$$Ln\gamma_i^R = q_i\left[1 - Ln\left(\sum_{j=1}^{C}\Theta_j \tau_{ji}\right) - \sum_{j=1}^{C}\left(\frac{\Theta_j \tau_{ij}}{\sum_{k=1}^{C}\Theta_k \tau_{kj}}\right)\right] \text{------------- (6)}$$

Here γ_i^C is the combinatorial part of the activity coefficient, γ_i^R the residual part of the activity coefficient, τ_{ij} is the adjustable parameter in the UNIQUAC equation, and χ_i is the equilibrium mole fraction of component i, the parameter Φ_i & Θ_i are given by:-

Segment fraction $\quad \Phi_i = \dfrac{\chi_i \tau_i}{\sum_{i=1}^{C}\chi_i \tau_i}$ -------------- (7)

Area fraction $\qquad \Theta_i = \dfrac{q_i \chi_i}{\displaystyle\sum_{i=1}^{C} q_i \chi_i}$ ---------------- (8)

$$\tau_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \quad \text{------ (9)}$$

Where, z---lattice coordination number

$\qquad r_i$ ---number of segments per molecule

$\qquad q_i$ ---relative surface area per molecule

The extended UNIQUAC model is described by Nicolaisen et al (1993) for aqueous electrolyte systems. It is derived from the original model (Abrams and Prausnitz ,1975 ;Maurer and Prausnitz ,1978) by adding a Debye-Huckel term(sander et al,1986) to take into account the presence of the ionic species in the mixture. The only parameters for the extended UNIQUAC model are the UNIQUAC interaction parameters and volume and surface area parameters.

2.3.2 UNIFAC GROUP CONTRIBUTION METHOD

The UNIFAC group contribution method (Fredenslund et al, 1975, 1977) is a broadly used tool for the prediction of liquid phase activity coefficients parameterized for a wide range of structural groups (Hansen et al ,1991). The empirical modification of the UNIFAC group contribution is the UNIFAC-Dortmund model, as developed by Gmehling et al (1993).

In UNIFAC model, the activity coefficients of a molecular component i (γ_i) in a multi component mixture are expressed as sum of two contributions: a combinatorial part (C), accounting for size and shape of the molecules and a residual part (R), a result of inter-molecular interactions.

$$Ln\gamma_i = Ln\gamma_i^C + Ln\gamma_i^R \quad \text{------------------- (1)}$$

The original UNIFAC is modified to Dortmund version by including ¾ exponents in the calculation of volume fraction.

$$Ln\gamma_i^C = Ln\left(\frac{\Phi_i'}{\chi_i}\right) + 1 - \frac{\Phi_i'}{\chi_i} - 0.5q_i\left(1 - \frac{\Phi_i}{\Theta_i} + Ln\frac{\Phi_i}{\Theta_i}\right) \quad \text{------------- (2)}$$

Where,　　$\Phi'_i = \dfrac{\chi_i r_i^{\frac{3}{4}}}{\sum\limits_j \chi_j r_j^{\frac{3}{4}}}$ ---------------- (3)

$\Theta_i = \dfrac{q_i \chi_i}{\sum\limits_j q_j \chi_j}$ ---------------- (4)

$\Phi_i = \dfrac{\chi_i r_i}{\sum\limits_j \chi_j r_j}$ ---------------- (5)

$q_i = \sum\limits_k v_k^i Q_k$ ---------------- (6)

Where, χ_i ----- mole fraction of the component i

v_k^i -----no. of groups of type K in molecule I .

The residual part is given by the solution of groups concept, expressed by

$Ln\gamma_i^R = \sum\limits_k v_k^i \left(Ln\gamma_k - Ln\gamma_k^i \right)$ ------------- (7)

Where, γ_k ---- Group residual activity coefficient.

γ_k^i ---- Group residual activity coefficient for reference solution.

$Lnv_k = Q_k \left[1 - Ln\left(\sum\limits_m \Theta_m \psi_{mk} \right) - \sum\limits_m \dfrac{\Theta_m \psi_{km}}{\sum\limits_n \Theta_n \psi_{nm}} \right]$ -------------- (8)

The residual part remains unchanged compressing with the original UNIFAC, except the energy parameters, ψ_{mn} is correlated by a more complex expression for the temperature dependence.

$\psi_{mn} = \exp\left(-\dfrac{A_{mn} + B_{mn}T + C_{mn}T^2}{T} \right)$ ---------------- (9)

$\Theta_m = \dfrac{Q_m \chi_m}{\sum\limits_n Q_n \chi_n}$ ---------------- (10)

The parameters A_{mn}, B_{mn} and C_{mn} in the above expression have been fitted by Gmehling et al (1993) using liquid-liquid equilibrium data.

2.3.3 NRTL MODEL(Non-random two liquid Model)

The model NRTL (non-random two liquid) by Renon and Prausnitz for the activity coefficient is based on the local composition concept and it is applicable for partially miscible systems. In order to take into account the salt effect on liquid-liquid equilibrium, the original NRTL model has been empirically extended. The extended NRTL model is given by:-

$$Ln\gamma_i = \frac{\sum_j \tau_{ji} G_{ji} \chi_i}{\sum_k G_{ki} \chi_k} + \sum_j \frac{\chi_j G_{ij}}{\sum_k G_{kj} \chi_k} \left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} \chi_k}{\sum_k G_{kj} \chi_k} \right) \text{-------------- (1)}$$

$$\tau_{ij} = \frac{g_{ij}}{RT} = A_{ij} + \frac{B_{ij}}{T} \qquad \text{----------------- (2)}$$

$$g_{ij} = \exp\left(-\alpha_{ij} \tau_{ij}\right) \qquad \text{------------------ (3)}$$

$$\alpha_{ij} = \alpha_{ji} \qquad \text{------------------ (4)}$$

In equations (1) to (3), g_{ij} represents the energy interactions between compounds i and j, while α_{ij} is a non-randomness parameter that derives from the local composition assumption. Thus, there are 5 adjustable parameters for each pair of substances: $A_{ij}, A_{ji}, B_{ij}, B_{ji}$ and α_{ij}. These parameters can be estimated with experimental data.

A large amount of experimental data was used to determine the NRTL energy interaction parameters. For the interactions of binary liquid-liquid the experimental data Othmer et al, Mc Cants et al, Matsumoto and Sone, Raja Rao and Venkata Rao, Venkataratnam et al, Petritis and Geankoplis, Ababi et al, Smirnova and Morachevskii, Lesteva et al, Krupatkin and Glagoleva, Iguchi and Fuse, De Santies et al, Kaczmarik and Radecki, Tegtmeier and Misselhorn, Marangirs et al, Ruiz et al, Letcher et al, Nakayama et al, Spottke et al, Esquivel and Bernardo-Gil and Letcher and Suswana were used with a total of 57 tie-lines. These data were available from the Dortmund Data Bank.

The estimation procedure is based on the Simplex method and Maximum Likelihood principle and consists in the minimization of the objective function S.

$$S = \sum_{K}^{D} \sum_{j}^{N_K} \left\{ \left(\frac{T_{jk} - T_{jk}^m}{\sigma T_{jk}} \right)^2 + \sum_{i}^{C_{k-1}} \left[\left(\frac{\chi_{ijk}^1 - \chi_{ijk}^{1m}}{\sigma \chi_{ijk}} \right)^2 + \left(\frac{\chi_{ijk}^{11} - \chi_{ijk}^{11,m}}{\sigma \chi_{ijk}} \right)^2 \right] \right\} \text{ ------------ (5)}$$

Where, D----- the number of data sets.

N_k--- the number of data points.

C_k--- the number of components in the data set K.

σ_{ijk}-- standard deviation in temperature.

$\sigma_{xijk}, \sigma_{xijk}^{11}$-----standard deviations in the composition of both liquid phases
at equilibrium.

2.3.4 WILSON MODEL

Wilson model was proposed by Wilson in 1964 and it was modified by Renon and Prausnitz, (1969). The Wilson equations are as follows:-

$$Ln\gamma_1 = C\left[-Ln(X_1 + \Lambda_{12}X_2) + \frac{\Lambda_{12}X_2}{X_1 + \Lambda_{12}X_2} - \frac{\Lambda_{21}X_2}{X_2 + \Lambda_{21}X_1} \right] \text{ ------------ (1)}$$

$$Ln\gamma_2 = C\left[-Ln(X_2 + \Lambda_{21}X_1) + \frac{\Lambda_{21}X_1}{X_2 + \Lambda_{21}X_1} - \frac{\Lambda_{12}X_1}{X_1 + \Lambda_{12}X_2} \right] \text{ ------------ (2)}$$

Where, $\Lambda_{12} = \dfrac{V_2}{V_1} \exp\left(\dfrac{-\Delta\lambda_{12}}{RT} \right)$ ------------- (3)

$\Lambda_{21} = \dfrac{V_1}{V_2} \exp\left(\dfrac{-\Delta\lambda_{21}}{RT} \right)$ ------------- (4)

V_1, V_2 ----molar liquid volumes.

$\Delta\lambda_{12}, \Delta\lambda_{21}$ ---- adjustable energy parameters.

C--------- adjustable binary parameter, usually set equal to unity.

2.3.5 DEBYE-HUCKEL MODEL

The Debye-Huckel model (Debye and Huckel, 1924) was the first model to describe long-rangeinteractions of the ions and it still is the commen element of many electrolyte models. The Debye-Huckel model can be derived either from electrostatics (Poisson equation) or from classical mechanics. In the Debye-Huckel theory the ions are point charges and the solvent is replaced by a dielectric continuum, according to the Mc Millan Mayer theory. For charged hard spheres the interaction potential U_{ij} between ion 1 and 2 is given by coulomb interaction.

$$U_{ij} = \frac{Z_i Z_j e^2}{\sum r_{ij}}$$

Where , e---charge of one electron.

Z---valence of the ion.

Σ--Dielectric constant.

The Boltzmann`s distribution law is inserted into Poisson`s equation, which is a relation between the distribution of charges and the electrostatic potential Ψ. The resulting equation is called Poisson-Boltzmann equation and describes the distribution of charge around an ion by assuming a Boltzmann distribution.

$$\nabla^2 \Psi(r) = -\frac{1}{\varepsilon} \sum_i Z_i e \rho_i \exp\left(\frac{Z_i e \Psi(r)}{KT}\right)$$

The Debye-Huckel theory further assumes that $KT >> Z_i e\Psi$, so that the exponential term can be linearized.

$$\nabla \Psi(r) = K^2 \Psi(r)$$

$$K^2 = \frac{e^2}{\varepsilon KT} \sum_i \rho_i Z_i^2 = \frac{2I}{\varepsilon KT}$$

Where K-----Debye-Huckel Shielding parameter.

I------Ionic strength.

The expression for activity coefficient is written as

$$Ln\gamma_i = -\frac{Z_i^2 e^2 \kappa}{8\pi\varepsilon KT}$$

2.3.6 Extended Debye-Huckel

The charged density with in a radius `Q` from the centre of the ion is assumed to be 0, resulting in---

$$Ln\gamma_i = -\frac{Z_i^2 e^2}{8\pi\varepsilon} \frac{\kappa}{KT(1 + \kappa a)}$$

The radius `a` is referred to as the closest approach parameter and is treated as an empirical constant.

CHAPTER-3

PREVIOUS INVESTIGATIONS

3.1 PREVIOUS INVESTIGATIONS

Many authors have worked on this liquid-liquid extraction system. But few of them have worked on the salt effect on liquid-liquid extraction system. It is observed that the use of salt has proven advantageous. Although a relative few significant advances and developments in this field is reported at experimental level. In this review developments and trends are outlined with emphasis on existing correlation. The systems with the results obtained by different authors are listed below.

3.1.1 LIST OF SOME PREVIOUS INVESTIGATION ON LLE

TABLE—1

Sl No.	Authors	System studied	Results
1.	Alberto Arce, Hector Rodriguez, Oscar Rodriquez, Ana Soto.	Water+Methanol+ dibutyl ether.	The system was studied at different temperatures and correlated their experimental data with UNIQUAC and NRTL model. UNIQUAC model led to better results. It was found that this method gives a relatively good prediction of liquid-liquid equilibrium of the system, but not good enough for many practical purposes.
2.	H. Ghanadzadeh, A. Ghanadzadeh.	Water + 2-ethyl-1-hexanol + Ethanol	The optimum UNIQUAC inter -action parameters between water, ethanol and 2-ethyl-1-hexanol were determined using the experimental data. The average RMSD value between observed and calculated mole

			fractions with a reasonable error was 1.70 % for the UNIQUAC model. The solubility of water in 2-ethyl-1-hexanol increases with amounts of ethanol added to water + 2-ethyl-hexanol.
3.	H. Ghanadzadeh Gilani, G. Khiati, A. K. Haghi.	2, 3-butanediol + 2-ethyl-hexanol + water.	The system was studied at different temperatures (300 .2, 305.2, 310.2,315.2K). The UNIQUAC model was used to correlate the experimental data. The average RMSD value between observed and calculated mole fraction is 1.38%. The solubility of water in 2-ethyl hexanol increases with amounts of 2,3-butanediol added to water + 2-ethyl hexanol.
4.	Juan C. Asensi , Julia Molto , Maria del Mar Olaya, Francisco Ruiz.	1-propanol + 1-pentanol + water	The UNIQUAC model was correlated with the data. For the liquid phases in the liquid-liquid equilibrium mean absolute deviations (MAD) is 0.04 mole fraction. Therefore, a not too satisfactory correlation of the experimental temp-composition results was obtained with the model.
5.	Mohsen Mohsen-Nia.	Ethanol +toluene + n-decane + water.	The NRTL was used to correlate the experimental results and to calculate the phase compositions of studied mixture. The effect of temperature in extraction of toluene from n-decane at lower temprature. Selectivity coefficient is higher but distribution

			coefficient is lower, therefore in the practical extraction the optimum temperature can be considered.
6.	Suheyla Cehreli, Dilek Ozmen, Vmur Dramur.	1-propanol + water + solvent (Methyl acetate, ethyl acetate, n-propyl acetate).	The UNIFAC model gives better prediction for (water + 1-propanol + ethyl acetate) and (water + 1-propanol + n-propyl acetate) where as UNIQUAC was found more suitable for (water + 1-propanol + methyl acetate). It is apparent from the separation factors and experimental tie-lines that n-propyl acetate is found to be preferable solvent for separation of 1-propanol from aqueous solutions.
7.	S. Ismail Kirbaslar	Butyric acid + dodecanol + water.	The temperature had practically no effect on the size of immiscibility region at the different temperatures studied. The results showed that butyric acid was more readily soluble in the solvent-rich phase than in the water-rich phase.
8.	Suheyla Cehreli, Besir Tatli, Pelin Bagman.	Water + propionic acid + cyclo hexanone.	It was observed that the effect of the temperature changes on the shape and the size of the immiscibility gap were insignificant over the investigated range. Experimental tie lines data of this work were analyzed and predicted using UNIFAC model. The average RMSD value between the measured and calculated mass fraction was 0.08 for UNIFAC model.

9.	Hengde Li, Kazuhiro Tamura.	Ethanol + α-pinene + water.	The experimental results were well correlated by the modified UNIQUAC model having only binary parameters.
10.	Youn Yong Lee, Youn Woo Lee.	Water + Ter-butyl alcohol + Di-Isobutylene.	They studied the system at different temperatures and correlated their experimental data with NRTL and UNIQUAC model. They observed experimentally that as the temperature is increased, the solubility as well as area of heterogeneity increased with a minimum variation.
11.	Joseph W.Kovach Warren D. Selder.	Dibutyl ether + Water + Sec-Butyl alcohol.	They studied the system and correlated the experimental data independently by using the UNIQUAC model.
12.	Suheyla Cehreli, Dilek Ozmen, Besir Talli.	Water + propionic acid + diethyl phthalate.	The average RMSD value between the measured and calculated mass fraction was 0.03. It can be concluded that diethyl phthalate has high separation factor, very low solubility in water, high boiling point may be an adequate solvent to extract propionic acid from its dilute solutions.

3.1.2 LIST OF INVESTIGATIONS OF SALT EFFECT ON LLE

TABLE-2

Sl No.	Authors	System	Salt used	Results
1.	Fania S. Santos, Saul G.D`Avila, Martin Aznar.	Water+1-butanol + Acetone.	Sodium chloride, Sodium Acetate.	The effect of the salt addition on the original ternary systems was observed by the increase of the two-phase region and the changes in the slopes of the experimental tie-lines. Both salts have caused salting-out effect but the effect of sodium acetate is less than sodium chloride.
2.	HoracioN.Solimo, Carlos M.Bonatti, Monica B. Gramajo De Doz.	Water + propionic acid + 1-butanol.	Sodium chloride	Solubility and tie-line data were obtained at 303.2 K. The addition of salt enhanced significantly the distribution coefficient and selectivity's, while the region of heterogeneity increased as compared to the salt distribution. Tie-lines data were correlated by method of Othmer and Tobias and their parameters were evaluated.
3.	Kaj Thomsen, Maria C. Iliuta, Peter Rasmussen.	Water + alcohol.	Sodium chloride, KCl, Sodium sulphate.	The extended UNIQUAC model has been shown to be a good thermodynamic model for describing the complex phase behavior of mixed solvent systems containing one or more salts. The model only requires binary interaction parameters. These

				parameters are temperature dependent but composition independent.
4.	Milton A. P. Pereira, Martin Aznar.	Water+2-propanol +1 butanol.	Pota-ssium bromide, Magne-sium chloride	In general, both salts caused a salting out effect, but the effect of magnesium chloride is more than of potassium bromide. From the experimental data, activity coefficient was determined for the NRTL model. The parameters were estimated by using the simplex method.
5.	M. Govindarajan , P. L. Sabarathinam	Acetic acid + Methyl isobutyl ketone + water.	Sodium chloride, Sodium nitrate, Sodium sulphate, Zinc sulphate.	The Campbell correlation is modified to fit the data of salt containing ternary liquid system. The distribution data of these salts containing system have been correlated through the modified Nernst, Campbell and Eisen-joffe equations. Results based on modified Nernst equation show following order of salts zinc sulphate >sodium sulphate> sodium chloride>sodium nitrate.
6.	M. U. Pal, Madhusudan Rao.	Ethyl acetate + ethyl alcohol + water.	Pota-ssium acetate, sodium acetate.	Solubility and tie lines data in presence and absence of salt at 30ºC is determined. Potassium acetate system is more advantage over sodium acetate. Data on effect of same electrolytes on mutual solubility's of ethyl acetate

				and water at salt saturation at 30ºC also presented.
7.	M. M. Olaya, A. Botella, A. Marcilla.	Ethanol + water +1-pentanol	Sodium chloride.	The addition of salt to above system has following consequences; The 2liq quaternary region increases its size on addition of salt. It improves the distribution coefficient for ethanol extraction with 1-pentanol and selectivity also increases. It improves the ethanol extraction with 1-pentanol.
8.	T. C. Tan,K.K.D. D.S.Kannangara.	Water+1-propanol + methyl ether.	Pota-ssium chloride	Solubility and tie line data were obtained at 25ºC. Correlation was done by NRTL model. System was studied at higher salt concentration.
9.	Taher A. Al-sahhaf, Emina Kapetanovie Qadria Kadhem.	Water+2-butanone, Water + ethyl acetate.	KI,NaBr, LiCl.	The salts used have a greater salting out efficiency on ethyl acetate than on 2-butanone. Potassium iodide exhibits a salting in effect on 2-butanone and it appears that the salvation mechanism for KI is different from the other salts.
10.	T.C.Tan, S. Aravinth.	Acetic acid + 1-butanol+ water	NaCl, KCl	They studied the above system at different temperatures and correlated the data using NRTL model method and Eisen-joffe equation. Both salts show similar properties.

11.	V.Gomis,F.Ruiz,N.B oluda, M.D. Saquete.	Water+1-pentanol	Lithium chloride	The NRTL model satisfactorily correlates the data with low concentrations of LiCl. However when the concentration of salt raises, the model is unable to predict the increase in concentration of salt in the organic phase produced by the formation of solvate alcohol-salts.
12.	Xiaoping Lu , Pingfan Han , Yaming Zhang , Yanru Wang , Jun Shi.	Water + tertiary butanol	Pota-ssium fluoride	The separation of tertiary butanol from aqueous solution is feasible by salting out effect. The concentration of tertiary butanol increases slowly with an increasing salt.
13.	Water+	Water+n-butanol,n-propanol	Licl,NaBr,K Br	Salting out occurs at higher salt concentration, more amount of n-propanol is transferred to the butanol phase. Salotropic is not eliminated completely.

CHAPTER-4

EXPERIMENTAL PROCEDURE

4. EXPERIMENTAL PROCEDURE

4.1 INTRODUCTION

The experimental measurement of liquid-liquid equilibrium must accomplish 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 accomplished in one measurement, and in the other cases, two sets of measurements are necessary. In the first case, for a ternary system mixtures of three components are allowed to separate into its conjugate phases at equilibrium and the equilibria layers are analyzed for their composition which will give the end points of the tie lines. These endpoints when connected will give the bimodal curve. This method is called the method of analysis. The second method involves the estimation of binodal curve and the tie lines in two stages, which is measured separately.

4.2 EXPERIMENTAL SETUP

The experimental set up used for the determination of solubility data are as follows:-

A cell of 100ml capacity is taken. Here the temperature of the apparatus and the experimental fluid is controlled by a water jacket around the cell. The cell has two opening, one at the top and another at the bottom. Through the top opening the liquids are taken into the cell and during the experiment a thermometer is placed into it to record the temperature of the liquids. The bottom opening is the outlet for the liquids. A magnetic stirrer is provided for the sufficient agitation within the apparatus. The composition of the sample can be analyzed using the Gas Chromatography apparatus equipped with a thermal conductivity detector.

EXPERIMENTAL SETUP FOR LIQUID-LIQUID EXTRACTION
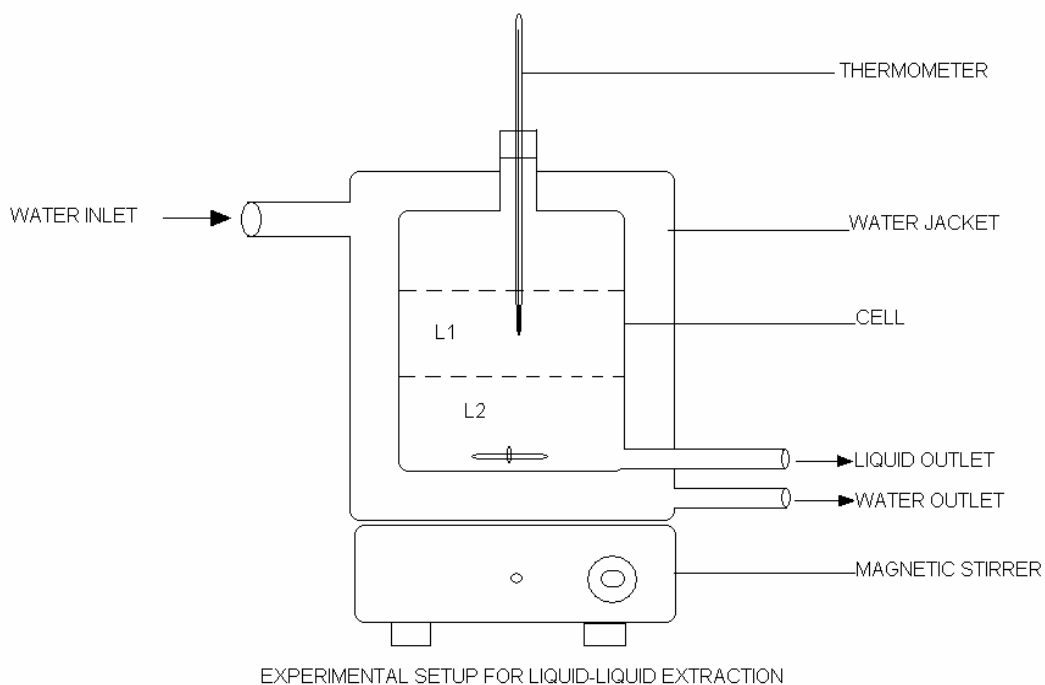
Fig.1 EXPERIMENTAL SETUP FOR LIQUID-LIQUID EXTRACTION

4.3 PROCEDURE FOR THE SYSTEM

The liquid-liquid measurements for the ternary system were made at atmospheric pressure in the temperature range of 300 to 325K. The preweighed amount of the mixture is taken in a 100ml jacketed cell. Then the other component is added and simultaneously the mixture is kept in constant agitation condition with the help of the magnetic stirrer. Water is continuously supplied to the jacketed cell to maintain the constant temperature. The mixture is stirred for 1-2 hours and then it is left to settle for 2-3 hours. After 2-3 hours the system gets separated into two phases. The top phase is taken out with the help of a syringe and the bottom phase is taken out through the bottom outlet. Then the samples are taken separately and analyzed in the Gas Chromatography. This procedure is repeated for the different amount of the liquids so as to cover the entire range of the composition.

4.4 PROCEDURE FOR THE SYSTEM WITH SALT

The experimental procedure for the determination of the solubility data of a salt containing ternary liquid system is similar to the procedure adopted for the salt free solution. The concentration of the aqueous salt solution is varied from 5% to20% of salt by mass. In this case the determination of the composition is not possible directly by Gas Chromatography due to the presence of the salt. So each layer (raffinate and extract) is taken or collected separately and each layer is boiled separately and condensed to make it salt free and then the composition of the sample is analyzed by using the Gas Chromatography.
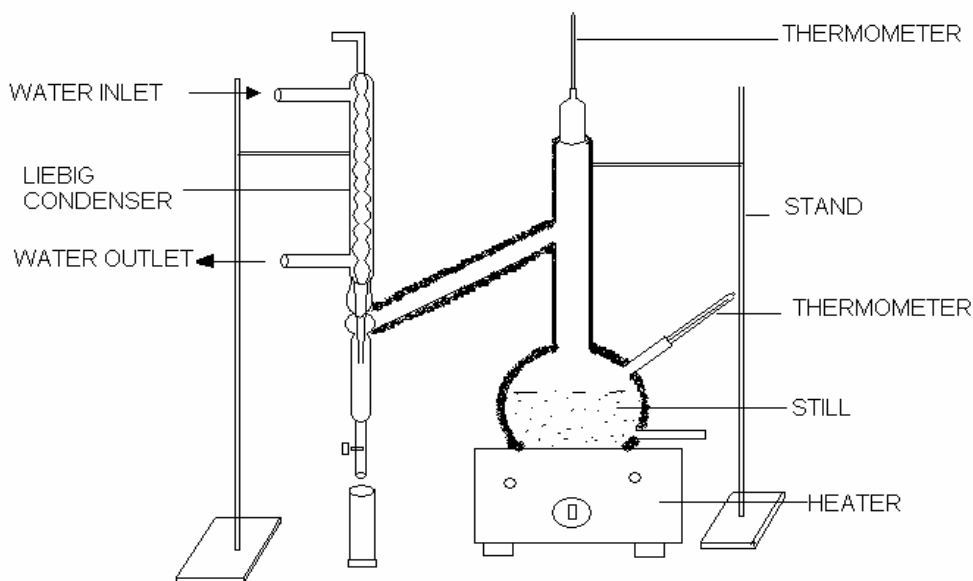
EXPERIMENTAL SETUP FOR EXTRACTING SALT FROM SAMPLE

Fig. 2 EXPERIMENTAL SETUP FOR EXTRACTING SALT FROM SAMPLE

4.5 METHOD OF ANALYSIS

The composition of the sample obtained from the liquid-liquid extraction can be analyzed by the following methods:-

4.5.1   TITRATION METHOD

In ternary liquid-liquid system, compositions of the coexisting phases were found by analyzing the concentration of the consulate component in each of the two phases. Known amounts of the two components and the dissolved salt corresponding to the points with in the binodial curve with contained in stoppered flasks, were agitated at constant temperature bath over a period of 2 hours. At the end of this period the flasks were allowed to remain in the bath until the phases had completely separated. Then the samples of the separated layers were withdrawn. Then the analysis is done by the simple titration method.

4.5.2   GAS CHROMATOGRAPH METHOD

Gas chromatograph consists of a flame ionization detector and electronic integrator. The injector and detector are maintained at constant temperature. A stainless steel with 10% squalane in chromosorb was used .Helium carrier gas was used with a constant flow rate at room temperature. Samples are alternatively withdrawn from the two phases with 1-µl chromatographic syringes and injected into the chromatograph. Calibration analyses are carried out to convert the peak area ratio to the weight composition of the mixture. In case of dissolved salts each layer was boiled separately and condensed to make it salt free and then analyses of each layer was carried out.

4.5.3   REFRACTIVE INDEX METHOD

In this the three components were agitated in a constant temperature bath over a period of 2 hours. At the end of this period the flasks were allowed to remain in the bath until the phases had completely separated. Then the samples of the separated layers were withdrawn and their refractive indexes were measured. The composition of the equilibrium layers were determined by references to a large scale plot of refractive index against solute concentration for saturated solution. In case of dissolved salts each layer was boiled separately and condensed to make it salt free and then refractive index of each layer was measured.

4.5.4   SPECIFIC-GRAVITY METHOD

Here similar procedure is followed as in other case. The separated layers were withdrawn and their specific gravities were measured. The compositions of the equilibrium layers were determined by references to a large-scale plot of specific gravity against solute

concentration for saturated solutions. In case of dissolved salts each layer is boiled separately and condensed to make it salt free and then specific gravity of each layer was measured.

4.6 CHROMATOGRAPHY

Chromatography involves a sample (or sample extract) being dissolved in a *mobile phase* (which may be a gas, a liquid or a supercritical fluid). The mobile phase is then forced through an immobile, immiscible *stationary phase*. The phases are chosen such that components of the sample have differing solubility's in each phase. A component which is quite soluble in the stationary phase will take longer to travel through it than a component which is not very soluble in the stationary phase but very soluble in the mobile phase. As a result of these differences in mobility's, sample components will become separated from each other as they travel through the stationary phase.

Gas Chromatography

Gas chromatography is the use of a carrier gas to convey the sample through a column consisting of an inert support and a stationary phase that interacts with sample components. Gas chromatography especially gas-liquid chromatography involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of the inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid.
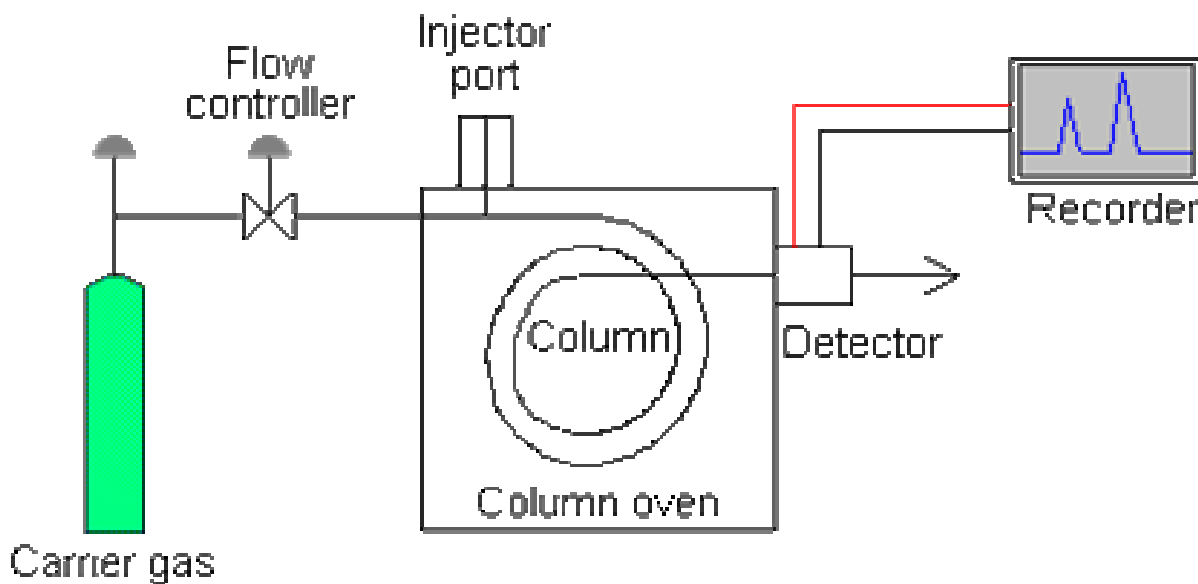
Fig.3 Diagram illustrating the Gas-Liquid Chromatography

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4.6.1 Instrumental components

- **Carrier gas**

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities.
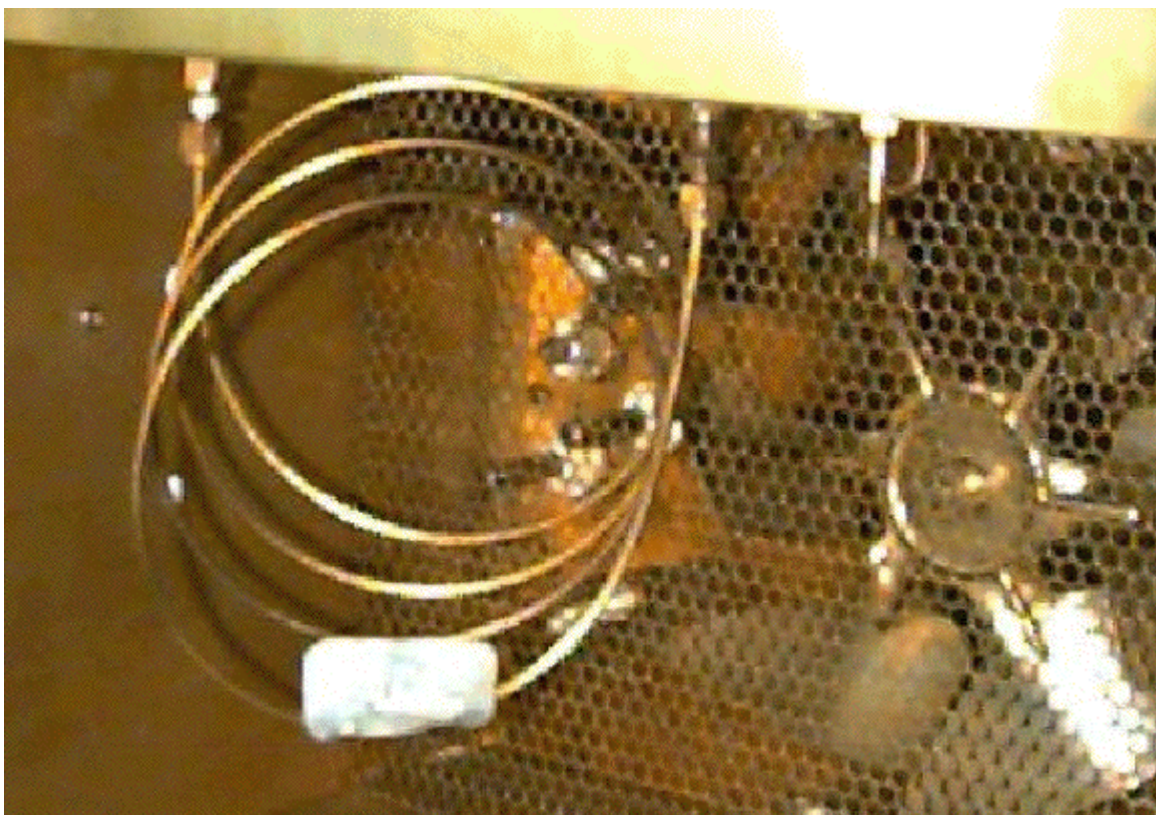
Fig 4 Steel column installed in Oven

- **Sample injection port**

For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a "plug" of vapour - slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a microsyringe is used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. The temperature of the sample port is usually about 50°C higher than the boiling point of the least volatile component of the sample. For packed columns, sample size ranges from

tenths of a micro liter up to 20 micro liters. Capillary columns, on the other hand, need much less sample, typically around 10^{-3}mL. For capillary GC, split/split less injection is used.

The injector can be used in one of two modes; split or split less. The injector contains a heated chamber containing a glass liner into which the sample is injected through the septum. The carrier gas enters the chamber and can leave by three routes (when the injector is in split mode). The sample vaporizes to form a mixture of carrier gas, vaporized solvent and vaporized solutes. A proportion of this mixture passes onto the column, but most exits through the split outlet. The septum purge outlet prevents septum bleed components from entering the column. Here is an illustration of a split/split less injector.

The split / splitless injector

- Rubber septum
- Septum purge outlet
- Carrier gas inlet
- Split outlet
- Heated metal block
- Vapourisation chamber
- Glass liner
- Column

Fig. 5 Injector

- **Columns**

There are two general types of column, packed and capillary (also known as open tubular). Packed columns contain a finely divided, inert, solid support material (commonly based on diatomaceous earth) coated with liquid stationary phase. Most packed columns are 1.5 - 10m in length and have an internal diameter of 2 - 4mm.Capillary columns have an internal diameter
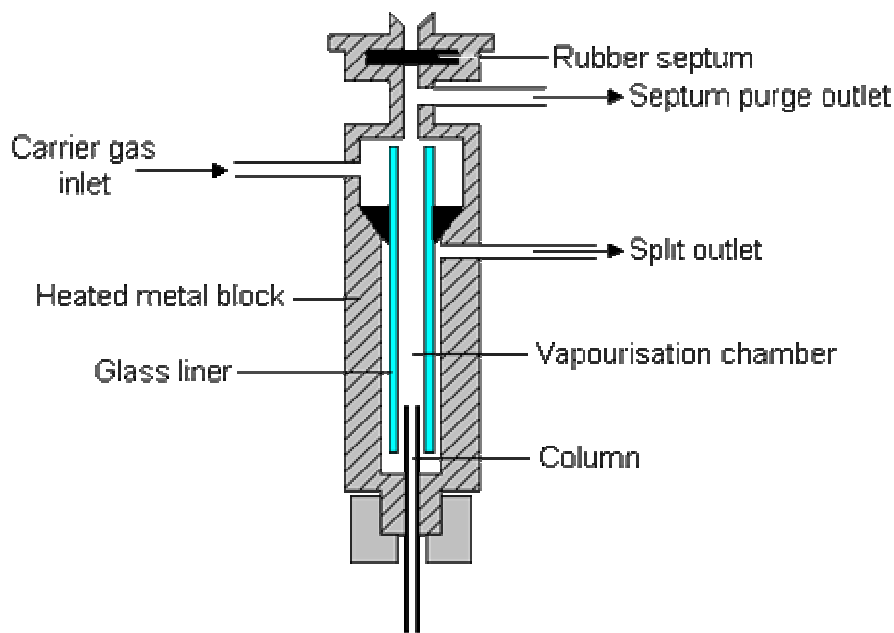
of a few tenths of a millimeter. They can be one of two types; wall-coated open tubular (WCOT) or support-coated open tubular (SCOT). Wall-coated columns consist of a capillary tube whose walls are coated with liquid stationary phase. In support-coated columns, the inner wall of the capillary is lined with a thin layer of support material such as diatomaceous earth, onto which the stationary phase has been adsorbed. SCOT columns are generally less efficient than WCOT columns. Both types of capillary column are more efficient than packed columns. In 1979, a new type of WCOT column was devised - the Fused Silica Open Tubular (FSOT) column;

Cross section of a Fused Silica Open Tubular Column

Polyimide coating
Fused silica tube
Chemically bonded stationary phase
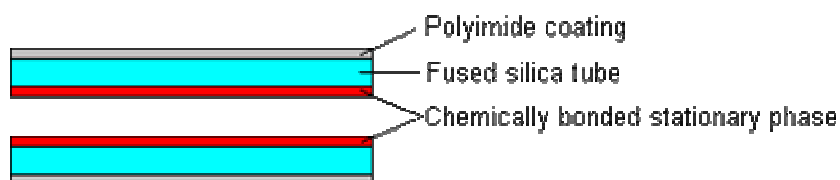
- **Column temperature**

For precise work, column temperature must be controlled to within tenths of a degree. The optimum column temperature is dependant upon the boiling point of the sample. As a rule of thumb, a temperature slightly above the average boiling point of the sample results in an elution time of 2 - 30 minutes. Minimal temperatures give good resolution, but increase elution times. If a sample has a wide boiling range, then temperature programming can be useful. The column temperature is increased (either continuously or in steps) as separation proceeds.

- **Detectors**

There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity. A non-selective detector responds to all compounds except the carrier gas, a selective detector responds to a range of compounds with a common physical or chemical property and a specific detector responds to a single chemical compound. Detectors can also be grouped into concentration dependant detectors and mass flow dependant detectors. The signal from a concentration dependant detector is related to the concentration of solute in the detector, and does not usually destroy the sample Dilution of with make-up gas will lower the detectors response. Mass flow dependant detectors usually destroy

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the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependant detector is unaffected by make-up gas.

The Flame Ionisation Detector
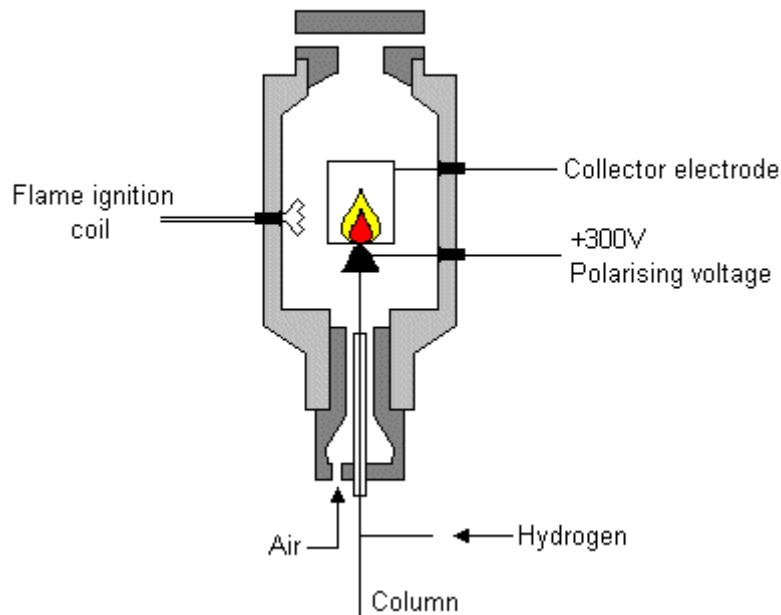
Fig.7 Flame Ionization Detector

The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is applied at the burner tip, and a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. FIDs are mass sensitive rather than concentration sensitive; this gives the advantage that changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds; it has high sensitivity, a large linear response range, and low noise. It is also robust and easy to use, but unfortunately, it destroys the sample.

CHAPTER-5

PRESENTATION OF RESULTS

5. PRESENTATION OF RESULTS

Experiments are conducted on the system Water + 1-propanol + Ethyl acetate with varying salt concentrations and varying temperatures. The basic objective of this project is to determine the best temperature range and the salt from NaCl and $(NH_4)_2SO_4$ which enhances the separation or extraction of the solute by the specified solvent. The experiments were conducted and the resulting extract and raffinate phase was analyzed with the help of the gas chromatography. The plots of voltage vs time was obtained from the gas chromatography, showing the percent volume of the different components present in both the phases. For each phase a separate plot is obtained.

Here we have considered two salts: NaCl and $(NH_4)_2SO_4$. We have tried to show the effect of these two salts on the system at temperatures 27ºC, 32ºC and 37ºC. Thus considering all these factors lot of experiments are conducted and lot of plots were obtained from the gas chromatography. But it is not possible to produce all these plots in this project. Thus we have attached some of the plots and the other plots are available in the department library. From these the volume of the different components present in each phase is calculated. These are tabulated in Table 5.1 and the equilibrium data's are tabulated in Table 5.2.Considering these data's the solubility curves and the equilibrium curves are plotted on the ternary plots. All salt containing data are reported on salt free basis. The experimental tie-line data under no salt condition were determined and presented in the respective Tables.

5.1 EMPIRICAL CORRELATION OF SALT EFFECT ON LIQUID-LIQUID EQUILIBRIUM

The presence of the dissolved salt in a liquid mixture is likely to bring about a change in the liquid structure by promoting, destroying or bringing about other interactions between the components. Also the forces involved and any changes caused by salt addition may differ from system to system and from salt to salt.

The effects of salt on liquid-liquid equilibria of a ternary system have been widely studied. Several theories have advanced to explain the complex effect. However, the mathematical characterization of the salt effect has been semi-quantitative at best, because of the limitations of the theories or inadequacy of assumption made in the derivation of those equations. Hand, Othmer and Tobias have proposed equations to correlate the tie-line data of ternary liquid-liquid systems under pure /no salt condition. Eisen and Joffe have proposed semi empirical models to correlate the tie-line data of the ternary liquid-liquid equilibrium under salt dissolved in the system. But the best method to correlate the tie-line data of the ternary liquid-liquid equilibrium under salt dissolved is the UNIQUAC Model(Universal quasi-chemical model) proposed by Abrams and Prausnitz and the UNIFAC group contribution method proposed by Fredenslund et al.

Fig.8 G. C. Analysis report for 10% NaCl (32ºC) Raffinate Phase 1

Fig.9 G. C. Analysis report for 10% NaCl (32ºC) Extract Phase 1

Fig.10 G. C. Analysis report for 10% NaCl (32ºC) Raffinate Phase 2

Fig.11 G. C. Analysis report for 10% NaCl (32ºC) Extract Phase 2

Fig.12 G. C. Analysis report for 10%NaCl (32ºC) Raffinate Phase 3

Fig.13 G. C. Analysis report for 10% NaCl(32ºC) Extract Phase 3

Fig.14 G. C. Analysis report for 10% Nacl(32ºC) 4

Fig.15 G. C. Analysis report for 10%(NH$_4$)$_2$SO$_4$ (32ºC) Raffinate Phase 1

Fig.16 G.C. Analysis report for 10 %(NH4)$_2$SO$_4$ (32ºC) Extract Phase 1

Fig.17 G. C. Analysis report for 10%$(NH_4)_2SO_4$ (32ºC) Raffinate Phase 2

Fig.18 G. C. Analysis report for 10%$(NH_4)_2SO_4$ (32ºC) Extract Phase 2

Fig.19 G. C. Analysis report for 10%(NH$_4$)$_2$SO$_4$ (32ºC) Raffinate Phase 3

Fig.20 G. C. Analysis report for 10 %(NH$_4$)$_2$SO$_4$ (32ºC) Extract Phase 3

Fig.21 G. C. Analysis report for 10%$(NH_4)_2SO_4$ (32ºC) 4

5.2 SOLUBILITY DATA

SYSTEM: WATER + 1-PROPANOL + ETHYL ACETATE

Table 5.2.1 No Salt (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
16.0	2.2	15.6	14.9	9.320	0.714	4.843	18.9	6.680	1.399	10.779
14.0	16.2	24.5	18.4	8.953	4.209	5.191	36.3	5.047	11.965	19.280
13.0	42.5	54.0	27.1	8.869	9.700	8.545	82.3	4.131	32.764	45.434
11.0	22.5	28.5	37.8	8.331	14.702	14.775	24.2	2.669	7.785	13.716
8.0	4.5	3.2								

Table 5.2.2 5% NaCl (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
10.8	1.0	25.3	12.4	9.428	0.772	2.200	24.7	1.372	0.228	23.100
10.0	7.5	26.7	15.4	7.660	4.448	3.292	28.8	2.340	3.052	23.408
10.3	15.1	23.3	22.1	8.274	8.883	4.943	26.6	2.026	6.217	18.357
4.2	11.0	10.3								

Table 5.2.3 10%NaCl (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
12.1	8.2	15.2	12.9	10.095	0.510	2.295	22.6	2.005	7.690	12.905
10.9	9.8	26.6	16.1	9.079	4.608	2.413	31.2	1.821	5.192	24.187
10.0	11.4	38.7	23.3	7.613	10.809	4.878	36.8	2.387	0.591	33.822
10.0	24.3	11.4								

Table 5.2.4 15%NaCl (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	6.7	26.6	15.2	12.098	0.431	2.671	32.1	1.902	6.269	23.929
13.0	17.6	23.0	20.8	10.316	7.545	2.939	32.8	2.684	10.055	20.061
15.0	37.6	25.8	28.1	10.231	14.791	3.078	50.3	4.813	22.927	22.560
7.0	20.3	7.4								

Table 5.2.5 No Salt (32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	0.9	25.8	19.9	12.800	0.542	6.558	20.8	1.200	0.358	19.242
14.0	14.6	25.5	25.0	11.185	7.086	6.729	29.1	2.815	7.514	18.771
13.0	21.0	22.2	38.3	10.812	12.598	4.890	27.9	2.188	8.402	17.310
8.0	17.2	14.3								

Table 5.2.6 5%NaCl (32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	1.1	34.5	17.7	12.397	0.474	4.829	31.9	1.603	0.626	29.671
14.0	13.5	34.0	23.9	11.514	8.062	4.324	37.6	2.486	5.438	29.676
12.0	21.7	25.8	23.5	8.165	10.129	5.206	36.0	3.835	11.571	20.594
9.0	22.3	14.1								

Table 5.2.7 10%NaCl (32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	1.1	38.4	16.1	13.097	0.357	2.646	37.4	0.903	0.743	35.754
13.0	15.0	25.3	22.1	9.543	9.458	3.099	31.2	3.457	5.542	22.201
12.0	26.6	21.4	26.5	8.311	13.368	4.821	33.5	3.689	13.232	16.579
9.0	24.8	20.9								

Table 5.2.8 15% NaCl(32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	13.2	31.2	16.1	13.019	0.796	2.285	43.3	1.981	12.404	28.915
14.0	21.9	20.6	21.1	11.832	6.831	2.437	35.4	2.168	15.069	18.163
13.0	28.7	11.5	25.9	8.901	13.856	3.143	27.3	4.099	14.844	8.357
9.0	23.7	5.0								

Table 5.2.9 No Salt(37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	1.2	41.1	20.0	11.250	0.576	8.174	37.3	3.750	0.624	32.926
13.0	10.7	19.6	23.0	10.886	6.932	5.182	20.3	2.114	3.768	14.418
11.0	19.2	18.6	21.5	7.282	9.375	4.843	27.3	3.718	9.825	13.757
8.0	17.6	11.2								

Table 5.2.10 5% NaCl(37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	1.2	28.2	18.3	12.415	0.533	5.352	25.1	1.585	0.667	22.848
14.0	13.3	29.5	22.9	11.547	6.729	4.624	33.9	2.453	6.571	24.876
12.0	21.8	19.4	24.8	8.250	12.680	3.870	28.4	3.750	9.120	15.530
8.0	18.8	8.4								

Table 5.2.11 10%NaCl(37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	6.2	24.8	17.9	14.423	1.125	2.352	28.1	0.577	5.075	22.448
14.0	23.7	32.4	20.3	10.342	7.247	2.111	49.8	3.658	16.453	29.689
12.0	31.5	18.0	17.6	7.683	15.982	3.935	33.9	4.317	15.518	14.065
7.0	26.4	14.4								

Table 5.2.12 15%NaCl(37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	7.3	17.6	15.1	12.431	0.558	2.111	23.8	1.569	6.742	15.489
13.0	19.5	19.3	21.5	11.767	6.730	3.003	30.3	1.233	12.770	16.297
12.0	36.5	16.7	30.0	8.839	18.723	2.438	35.2	3.161	17.776	14.262
7.0	29.5	10.6								

Table 5.2.13 5%$(NH_4)_2SO_4$ (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
16.0	1.0	27.1	18.9	15.074	0.429	3.397	25.2	0.926	0.571	23.703
15.0	10.6	28.0	25.3	11.908	6.246	7.146	28.3	3.092	4.354	20.854
12.0	22.0	23.0	30.5	8.302	14.077	8.121	26.6	3.698	7.923	14.879
8.0	19.0	16.8								

Table 5.2.14 10% $(NH_4)_2SO_4$ (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	0.9	24.4	19.2	13.949	0.546	4.705	21.1	1.051	0.354	19.695
14.0	11.3	28.5	24.0	12.528	5.234	6.238	29.8	1.472	6.066	22.262
12.0	19.1	18.9	28.3	9.768	12.307	6.225	21.7	2.232	6.793	12.675
8.0	18.7	13.9								

Table 5.2.15 15% $(NH_4)_2SO_4$ (27ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
16.0	6.2	27.1	19.1	14.034	0.583	4.483	30.3	1.966	5.617	22.617
15.0	17.5	29.4	24.4	12.414	6.314	5.672	37.5	2.586	11.186	23.728
13.0	28.3	19.1	28.4	9.720	13.592	5.088	32.0	3.280	14.708	14.012
8.0	23.1	11.7								

Table 5.2.16 5% $(NH_4)_2SO_4$ (32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	1.0	29.3	19.1	13.500	0.567	5.093	26.2	1.500	0.493	24.207
14.0	12.1	28.7	24.8	11.490	7.656	5.654	30.0	2.510	4.443	23.046
13.0	22.2	27.2	35.1	10.404	14.371	10.325	27.3	2.596	7.829	16.875
8.0	20.9	19.5								

Table 5.2.17 10% $(NH_4)_2SO_4$ (32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	1.1	33.2	18.0	13.142	0.496	4.362	31.3	1.858	0.604	28.838
14.0	12.7	21.0	23.7	12.093	6.599	5.008	24.0	1.907	6.101	15.992
12.0	21.2	17.2	29.8	9.551	13.907	6.342	20.6	2.449	7.293	10.858
8.0	18.9	12.3								

Table 5.2.18 15% $(NH_4)_2SO_4$ (32ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	5.7	16.9	16.3	12.592	0.492	3.216	20.3	1.408	5.208	13.684
14.0	21.3	24.7	21.4	11.419	6.474	3.507	38.6	2.581	14.826	21.193
12.0	25.9	18.9	23.4	8.869	10.939	3.592	33.4	3.131	14.961	15.308
8.0	26.0	13.3								

Table 5.2.19 5% $(NH_4)_2SO_4$ (37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	0.9	23.0	18.6	14.039	0.468	4.093	20.3	0.961	0.432	18.907
14.0	10.7	21.8	23.6	12.048	6.228	5.324	22.9	1.952	4.472	16.476
12.0	20.5	18.9	28.8	9.657	12.924	6.219	22.6	2.343	7.576	12.681
8.0	19.0	16.8								

Table 5.2.20 10%$(NH_4)_2SO_4$ (37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
15.0	6.5	25.9	17.4	13.035	0.579	3.786	30.0	1.965	5.921	22.114
15.0	17.7	27.5	24.8	13.141	7.113	4.546	35.4	1.859	10.587	22.954
12.0	30.1	23.6	30.3	9.103	16.199	4.998	35.4	2.897	13.901	18.602
8.0	30.8	15.5								

Table 5.2.21 15%$(NH_4)_2SO_4$ (37ºC)

Water	1-Prop	EA		RAFFINATE				EXTRACT		
				Water	1-Prop	EA		Water	1-Prop	EA
14.0	8.1	19.4	16.5	12.934	0.592	2.974	25.0	1.066	7.508	16.426
14.0	30.1	27.2	25.0	12.206	8.696	4.098	46.3	1.794	21.404	23.02
13.0	45.2	22.1	35.2	10.730	20.861	3.609	45.1	2.270	24.339	18.491
7.0	35.7	11.9								

5.3 EQUILIBRIUM DATA

Table 5.3.1 No Salt (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.87	0.02	0.11	0.21	0.01	0.78
0.78	0.11	0.11	0.22	0.14	0.64
0.64	0.21	0.15	0.28	0.24	0.48
0.51	0.27	0.22	0.32	0.28	0.40
0.42	0.29	0.29			

Table 5.3.2 5% NaCl (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.925	0.023	0.052	0.194	0.010	0.796
0.782	0.136	0.082	0.261	0.102	0.637
0.681	0.219	0.100	0.242	0.223	0.535
0.420	0.330	0.250			

Table 5.3.3 10%NaCl (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.934	0.014	0.052	0.269	0.309	0.422
0.822	0.125	0.053	0.197	0.168	0.635
0.632	0.269	0.099	0.221	0.016	0.763
0.498	0.363	0.139			

Table 5.3.4 15%NaCl (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.940	0.010	0.050	0.198	0.196	0.606
0.776	0.170	0.054	0.254	0.285	0.461
0.664	0.288	0.048	0.280	0.401	0.319
0.470	0.409	0.879			

Table 5.3.5 No Salt (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.879	0.011	0.110	0.200	0.018	0.782
0.748	0.142	0.110	0.292	0.234	0.474
0.685	0.239	0.076	0.245	0.283	0.472
0.481	0.310	0.209			

Table 5.3.6 5%NaCl (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.904	0.010	0.086	0.178	0.021	0.801
0.768	0.161	0.071	0.219	0.144	0.637
0.655	0.244	0.101	0.311	0.282	0.407
0.471	0.349	0.180			

Table 5.3.7 10%NaCl (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.946	0.008	0.046	0.092	0.023	0.885
0.727	0.216	0.057	0.329	0.158	0.513
0.616	0.297	0.087	0.316	0.340	0.344
0.418	0.346	0.236			

Table 5.3.8 15%NaCl (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.942	0.017	0.041	0.156	0.292	0.552
0.817	0.142	0.041	0.195	0.407	0.398
0.644	0.301	0.055	0.387	0.421	0.192
0.551	0.410	0.039			

Table 5.3.9 No Salt (37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.839	0.013	0.148	0.314	0.016	0.670
0.765	0.146	0.089	0.313	0.167	0.520
0.646	0.249	0.105	0.372	0.294	0.334
0.499	0.329	0.172			

Table 5.3.10 5% NaCl(37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.895	0.012	0.093	0.216	0.027	0.757
0.786	0.137	0.077	0.234	0.188	0.578
0.635	0.293	0.072	0.365	0.267	0.368
0.510	0.359	0.131			

Table 5.3.11 10%NaCl(37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.941	0.022	0.037	0.076	0.201	0.723
0.785	0.165	0.050	0.231	0.312	0.457
0.572	0.357	0.071	0.348	0.375	0.277
0.380	0.430	0.190			

Table 5.3.12 15%NaCl(37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.948	0.013	0.039	0.213	0.275	0.512
0.811	0.139	0.050	0.137	0.424	0.439
0.587	0.374	0.039	0.264	0.447	0.289
0.380	0.480	0.140			

Table 5.3.13 5%$(NH_4)_2SO_4$ (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.941	0.008	0.051	0.135	0.025	0.840
0.767	0.121	0.112	0.327	0.138	0.535
0.573	0.290	0.137	0.381	0.245	0.374
0.450	0.320	0.230			

Table 5.3.14 10% $(NH_4)_2SO_4$ (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.914	0.011	0.075	0.177	0.018	0.805
0.802	0.101	0.097	0.169	0.209	0.622
0.652	0.246	0.102	0.304	0.277	0.419
0.471	0.330	0.199			

Table 5.3.15 15% $(NH_4)_2SO_4$ (27ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.917	0.011	0.072	0.215	0.184	0.601
0.791	0.121	0.088	0.221	0.286	0.493
0.646	0.271	0.083	0.295	0.397	0.308
0.450	0.389	0.161			

Table 5.3.16 5% $(NH_4)_2SO_4$ (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.907	0.010	0.083	0.199	0.020	0.781
0.758	0.151	0.091	0.266	0.141	0.593
0.604	0.250	0.146	0.287	0.260	0.453
0.421	0.330	0.249			

Table 5.3.17 10% $(NH_4)_2SO_4$ (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.916	0.010	0.074	0.205	0.020	0.775
0.791	0.129	0.080	0.250	0.240	0.510
0.626	0.273	0.101	0.336	0.301	0.363
0.480	0.342	0.178			

Table 5.3.18 15% (NH$_4$)$_2$SO$_4$ (32ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.931	0.011	0.058	0.350	0.248	0.402
0.803	0.137	0.060	0.212	0.365	0.423
0.681	0.252	0.067	0.276	0.396	0.328
0.420	0.409	0.171			

Table 5.3.19 5% (NH$_4$)$_2$SO$_4$ (37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.925	0.009	0.066	0.169	0.023	0.808
0.792	0.123	0.085	0.267	0.184	0.549
0.642	0.257	0.101	0.304	0.295	0.401
0.450	0.320	0.230			

Table 5.3.20 10% (NH$_4$)$_2$SO$_4$ (37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0.923	0.012	0.065	0.215	0.195	0.590
0.802	0.130	0.068	0.175	0.299	0.526
0.599	0.320	0.081	0.250	0.334	0.416
0.381	0.440	0.821			

Table 5.3.21 15% (NH$_4$)$_2$SO$_4$ (37ºC)

RAFFINATE			EXTRACT		
Water	1-Propanol	EthylAcetate	Water	1-Propanol	EthylAcetate
0;935	0.013	0.052	0.146	0.308	0.546
0.809	0.173	0.018	0.130	0.464	0.406
0.601	0.350	0.049	0.161	0.519	0.320
0.339	0.520	0.141			
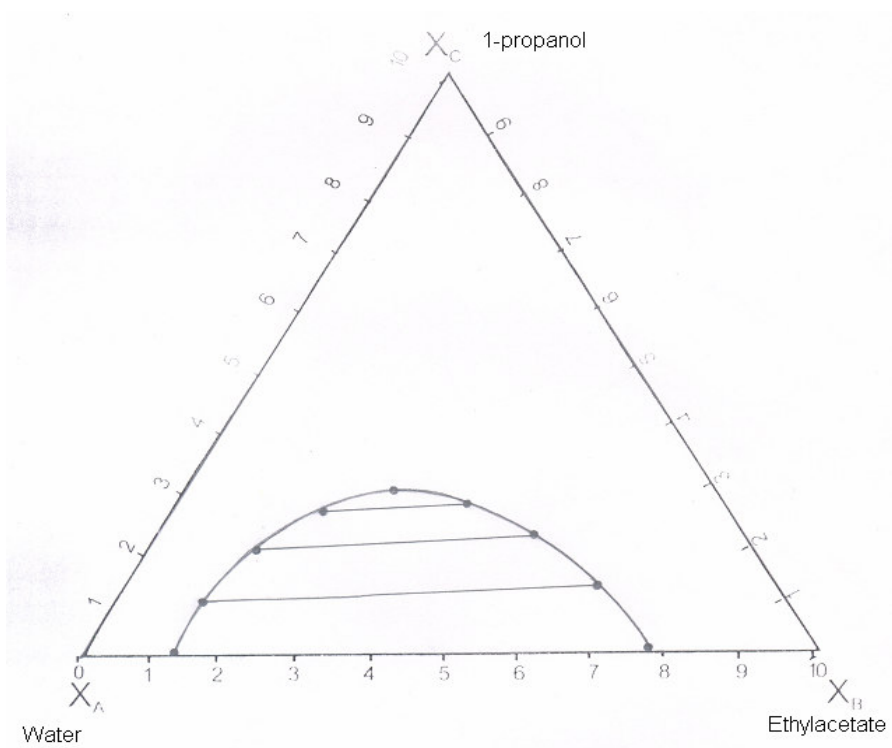
Fig. 22 Solubility curve for no salt (27ºC)
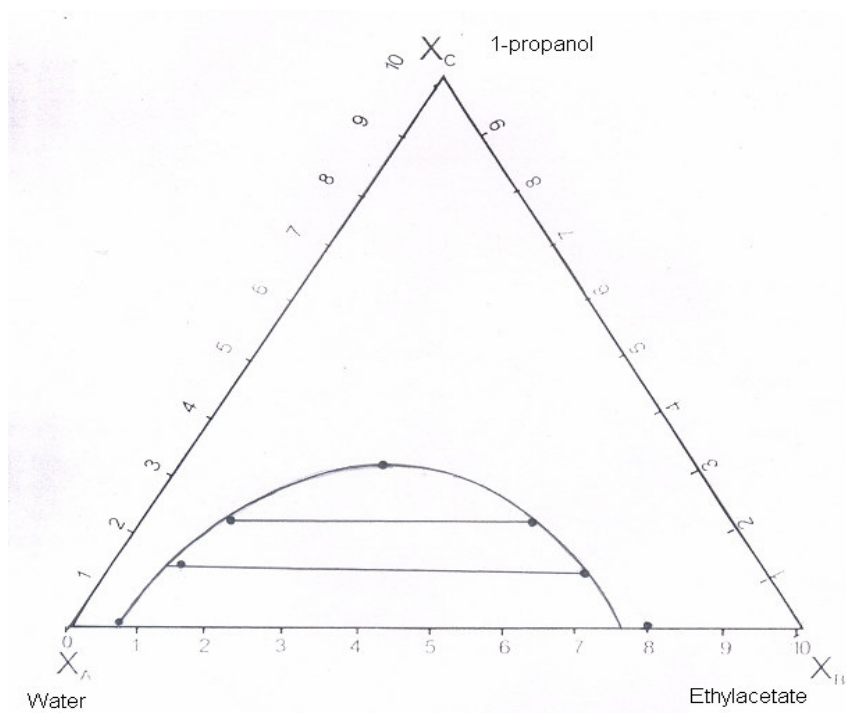
Fig.23 Solubility curve for 5% NaCl (27ºC)
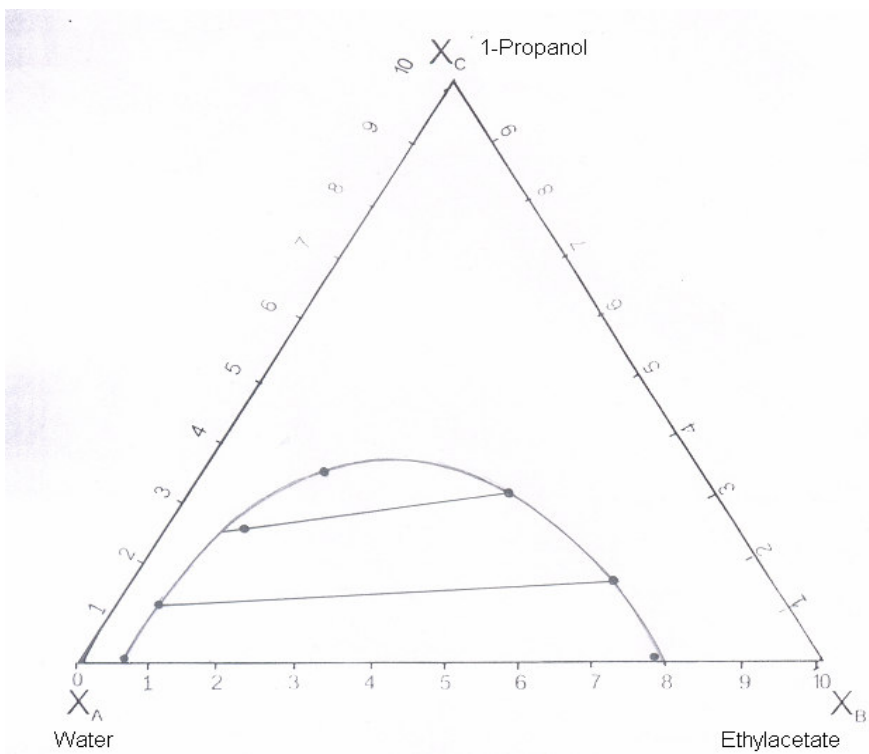
Fig.24 Solubility curve for 10%NaCl (27ºC)
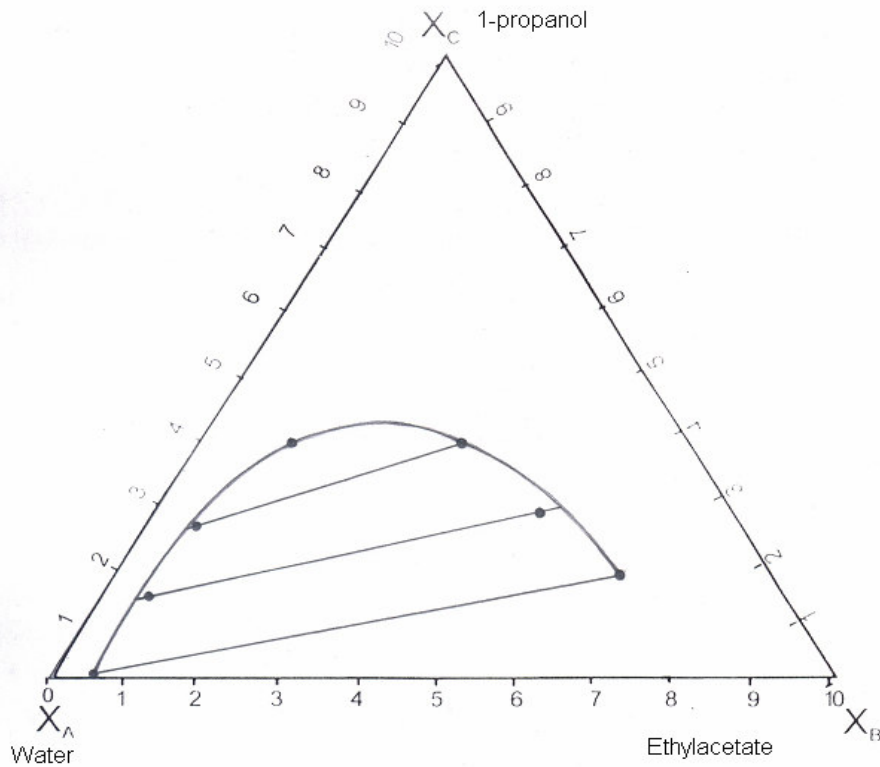
Fig.25 Solubility curve for 15% NaCl (27ºC)

66
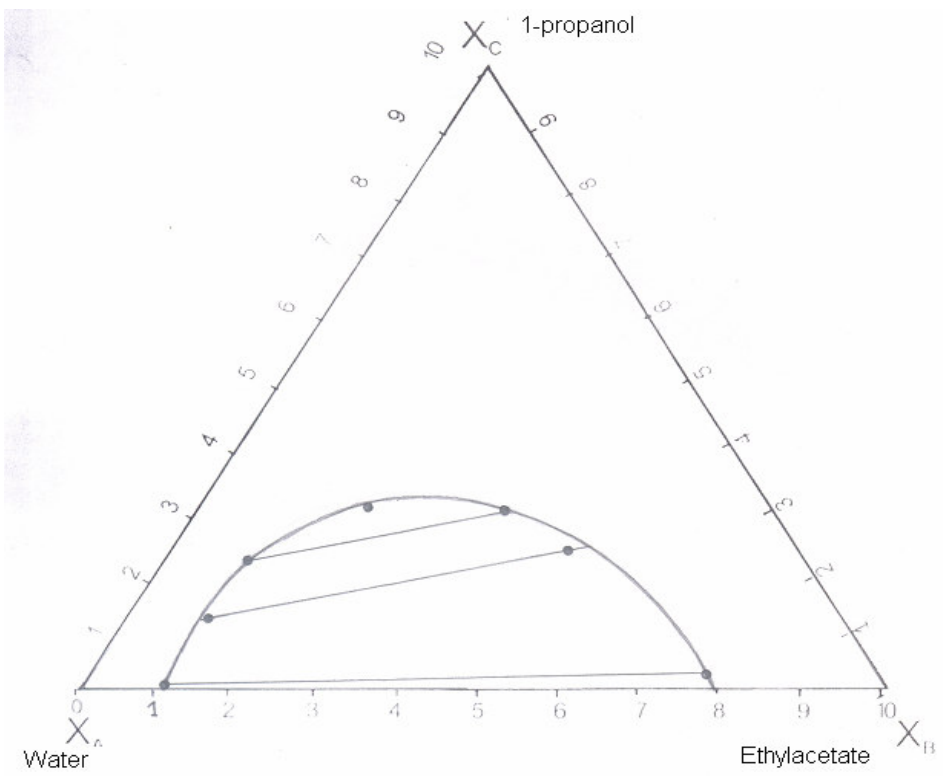
Fig.26 Solubility curve for no salt (32ºC)
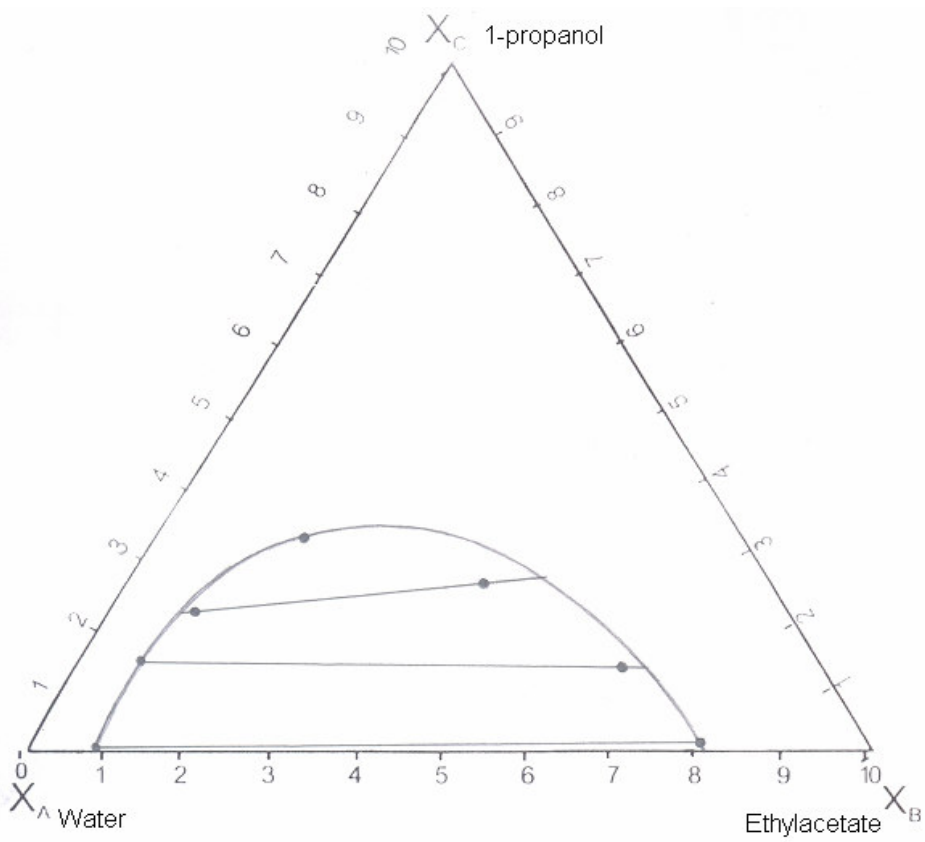
Fig.27 Solubility curve for 5% salt (32ºC)
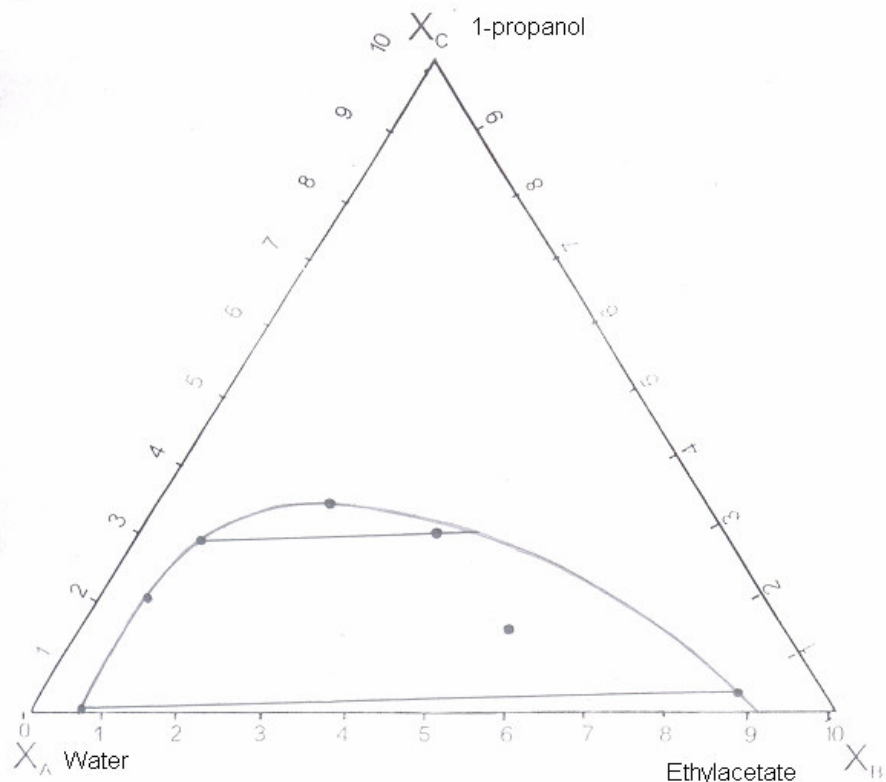
Fig.28 Solubility Curve for 10% NaCl (32℃)
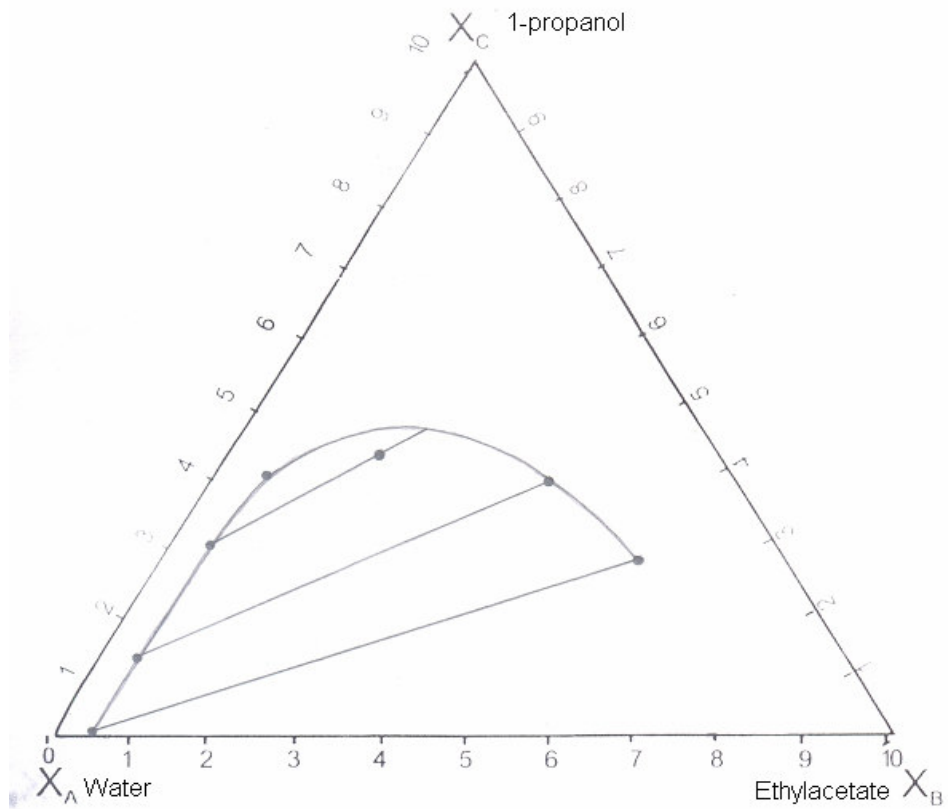
Fig.29 Solubility Curve for 15% NaCl (32℃)

68
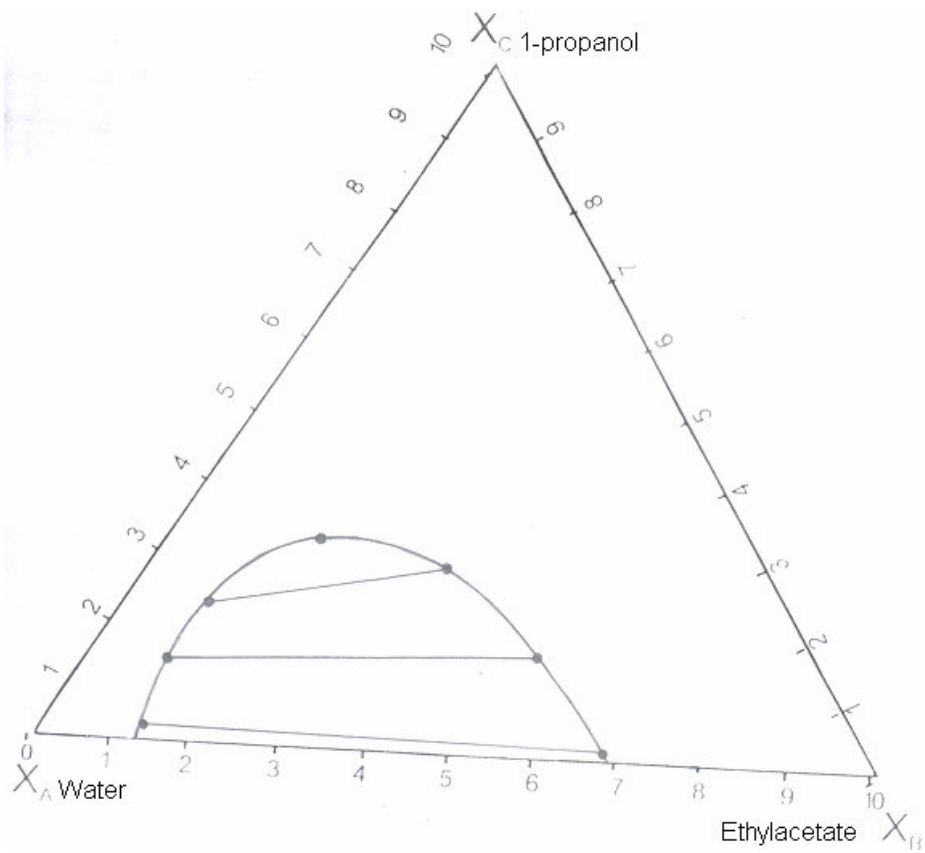
Fig.30 Solubility Curve for no salt (37ºC)
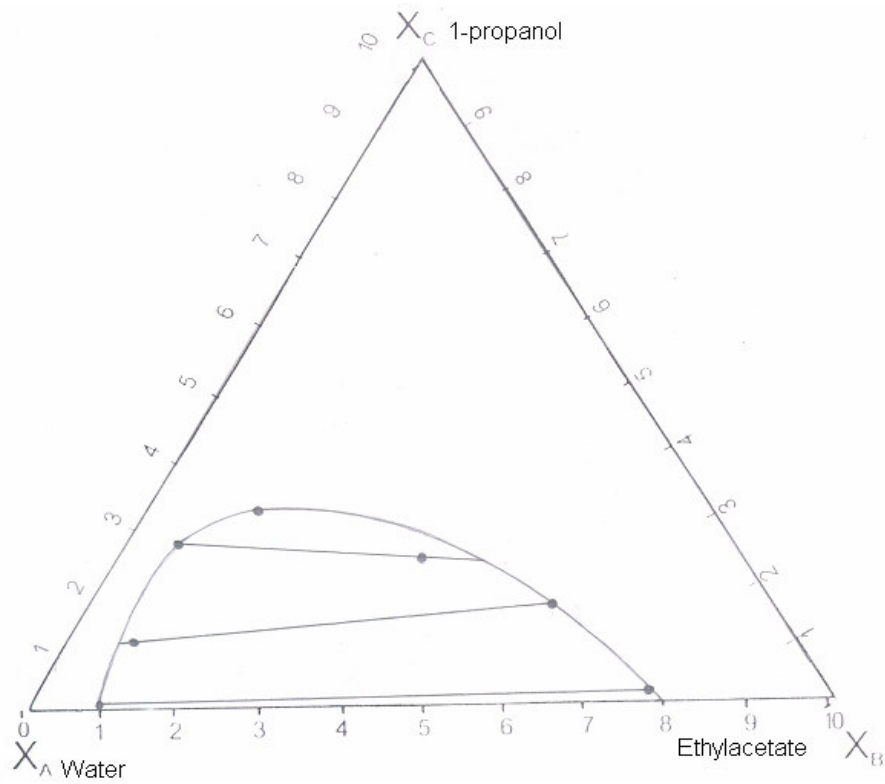
Fig. 31 Solubility Curve for 5% NaCl (37ºC)

69
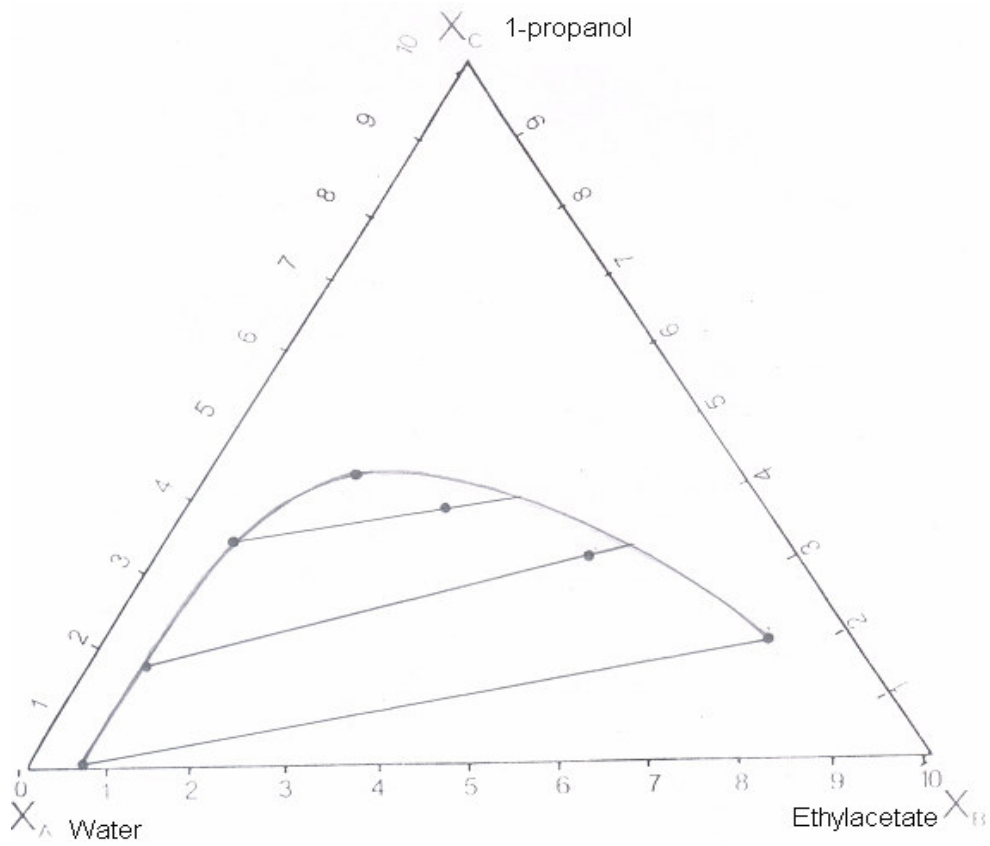
Fig. 32 Solubility Curve for 10% NaCl (37ºC)
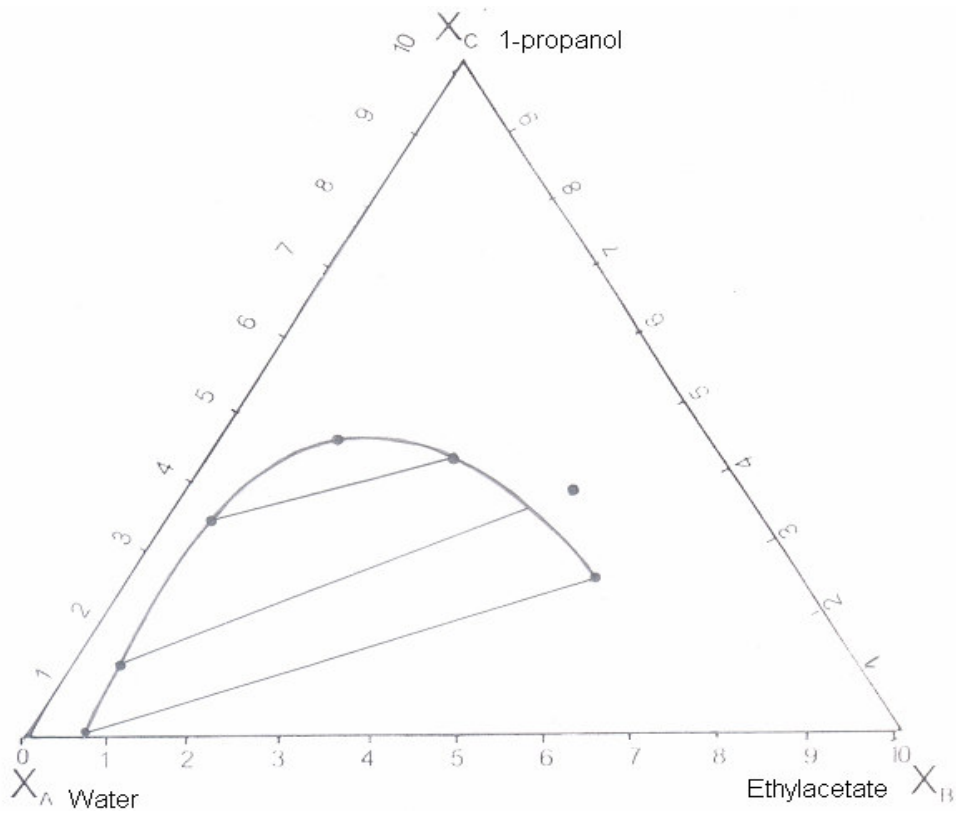
Fig. 33 Solubility Curve for 15% NaCl (37ºC)

70
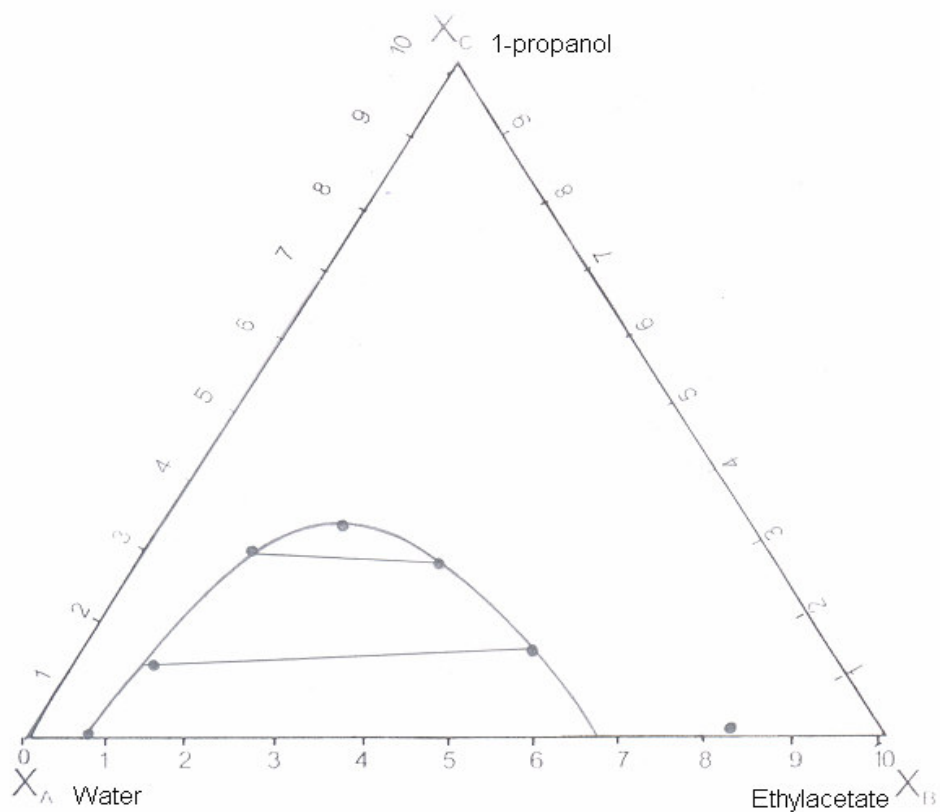
Fig. 34 Solubility Curve for 5% $(NH_4)_2SO_4$ (27ºC)
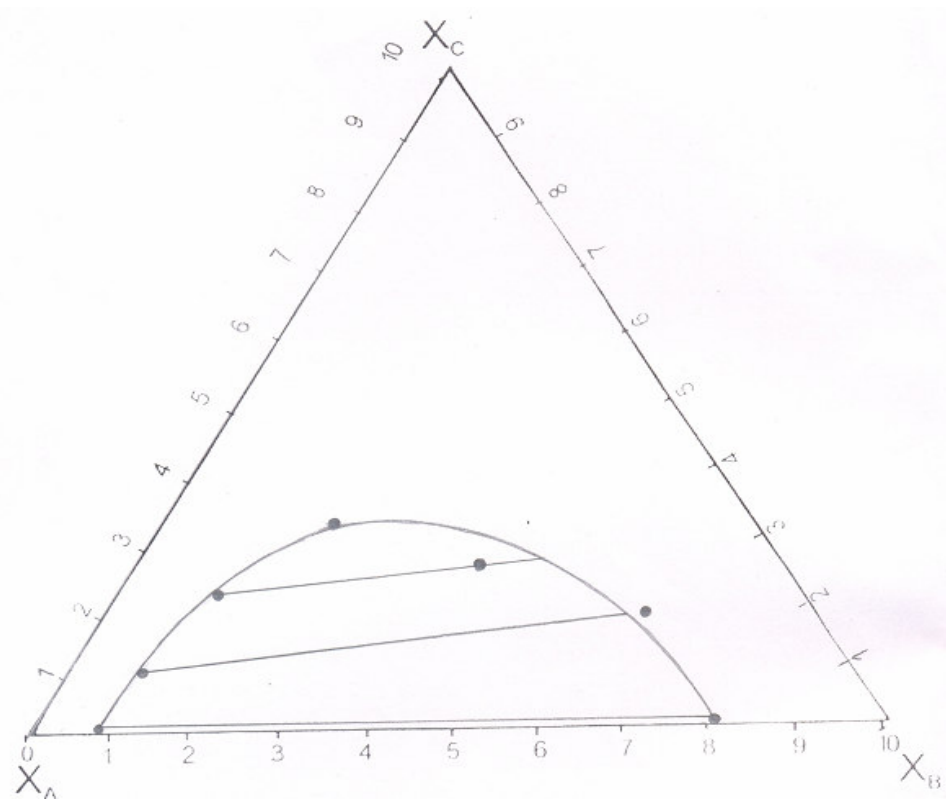
Fig. 35 Solubility Curve for 10%$(NH_4)_2SO_4$ (27ºC)

71
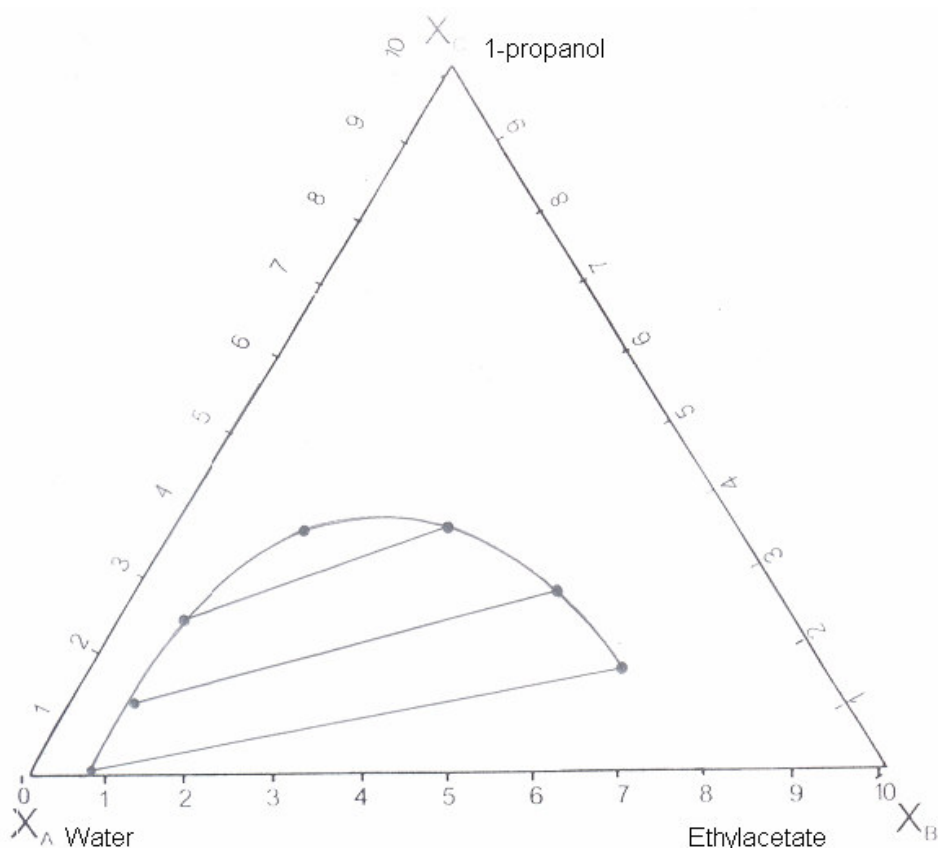
Fig. 36 Solubility Curve for 15% (NH$_4$)$_2$SO$_4$ (27ºC)
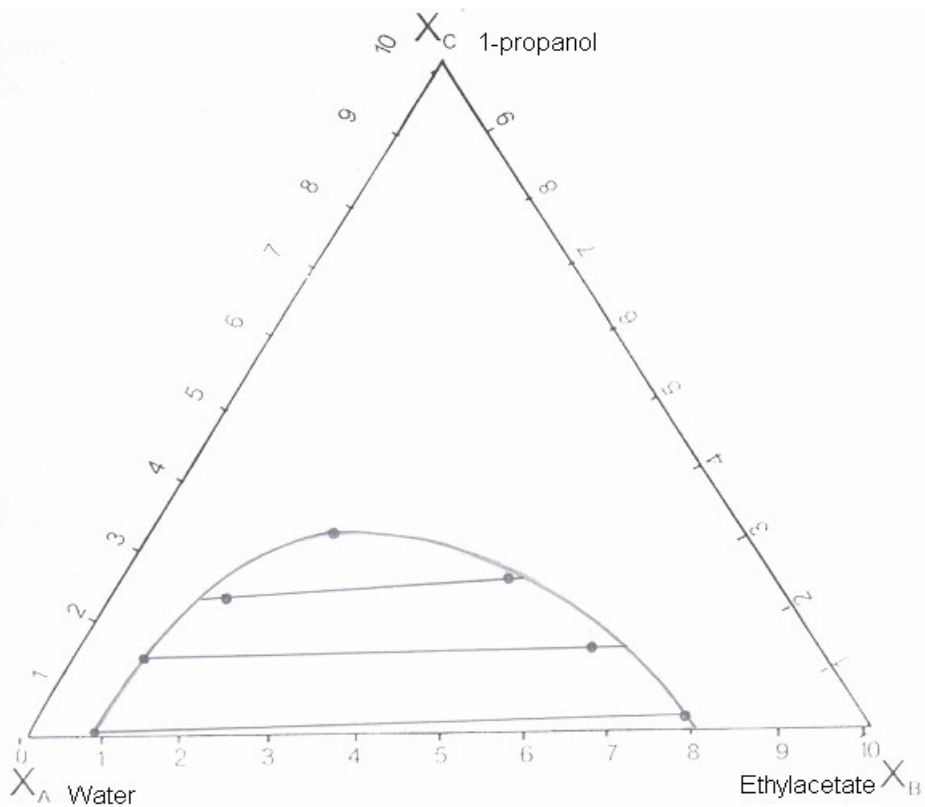
Fig. 37 Solubility Curve for 5% (NH$_4$)$_2$SO$_4$ (32ºC)

72
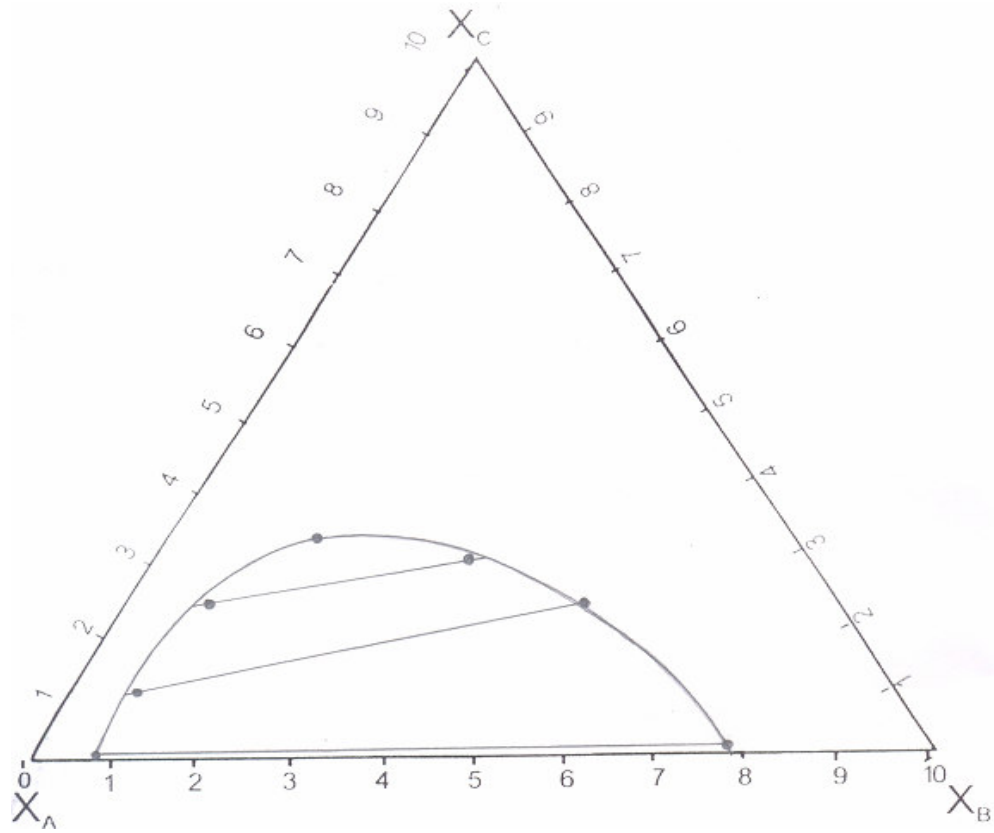
Fig. 38 Solubility Curve for 10%$(NH_4)_2SO_4$(32ºC)
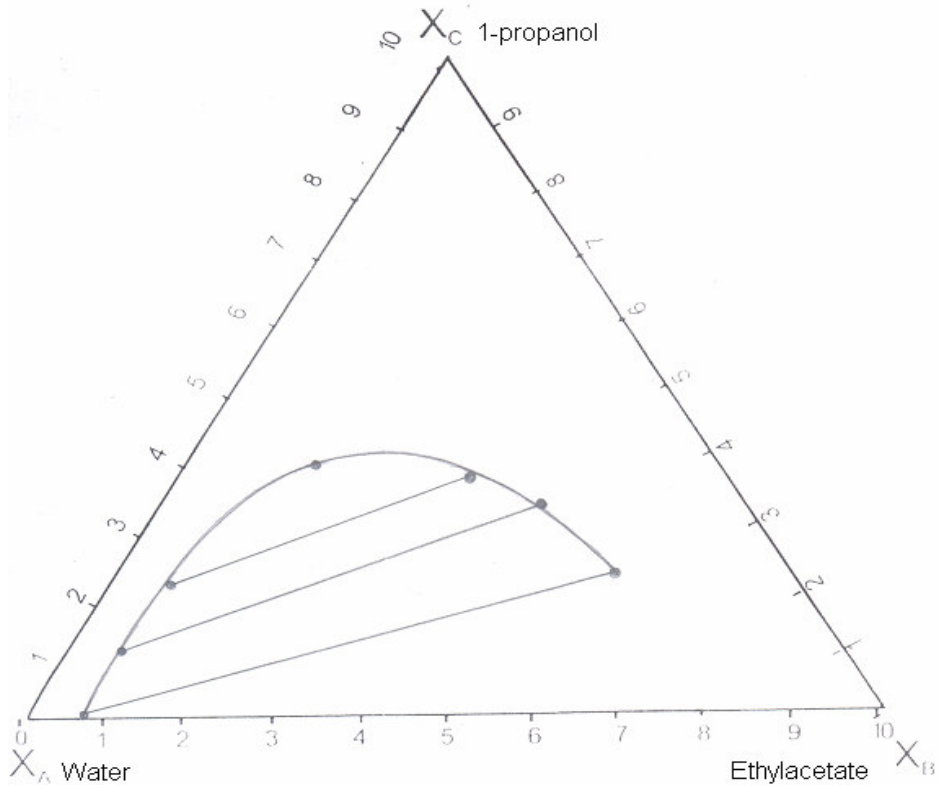
Fig. 39 Solubility Curve for 15% $(NH_4)_2SO_4$ (32ºC)
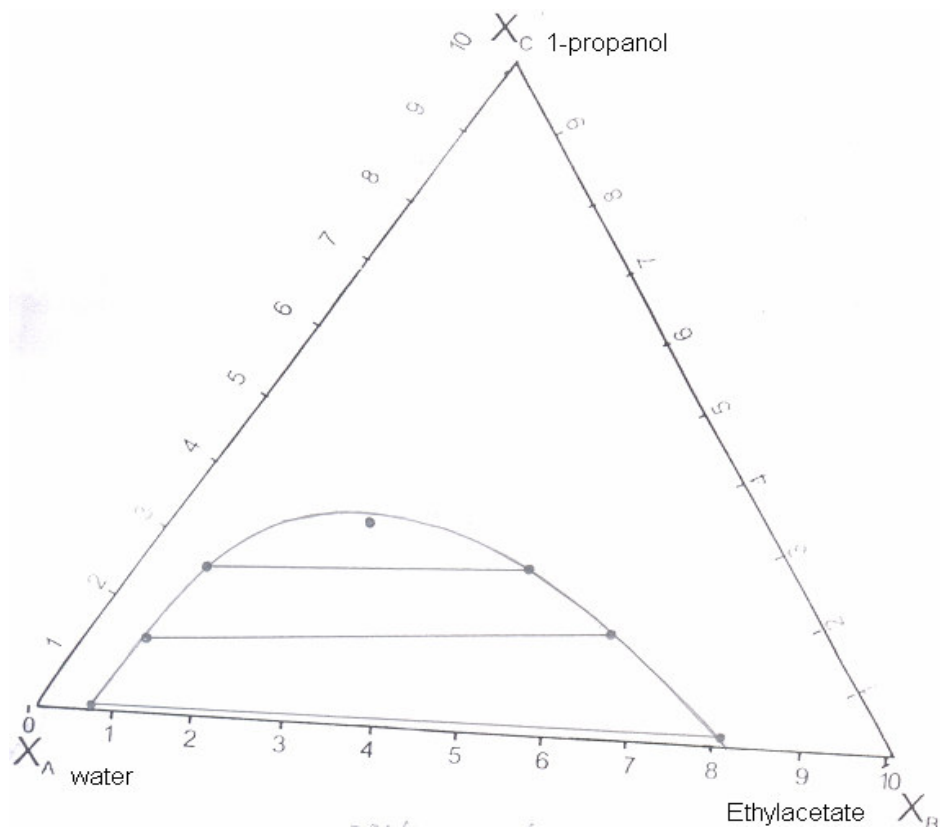
Fig. 40 Solubility Curve for 5% (NH$_4$)$_2$SO$_4$ (37ºC)
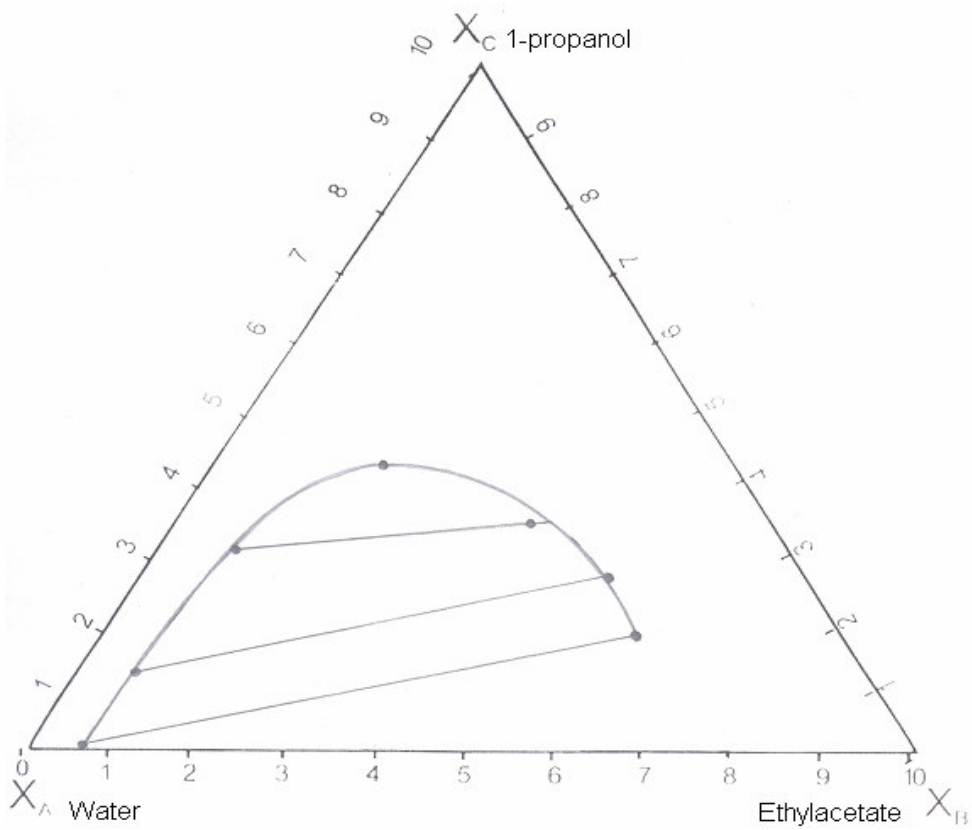
Fig. 41 Solubility Curve for 10% (NH$_4$)$_2$SO$_4$ (37ºC)
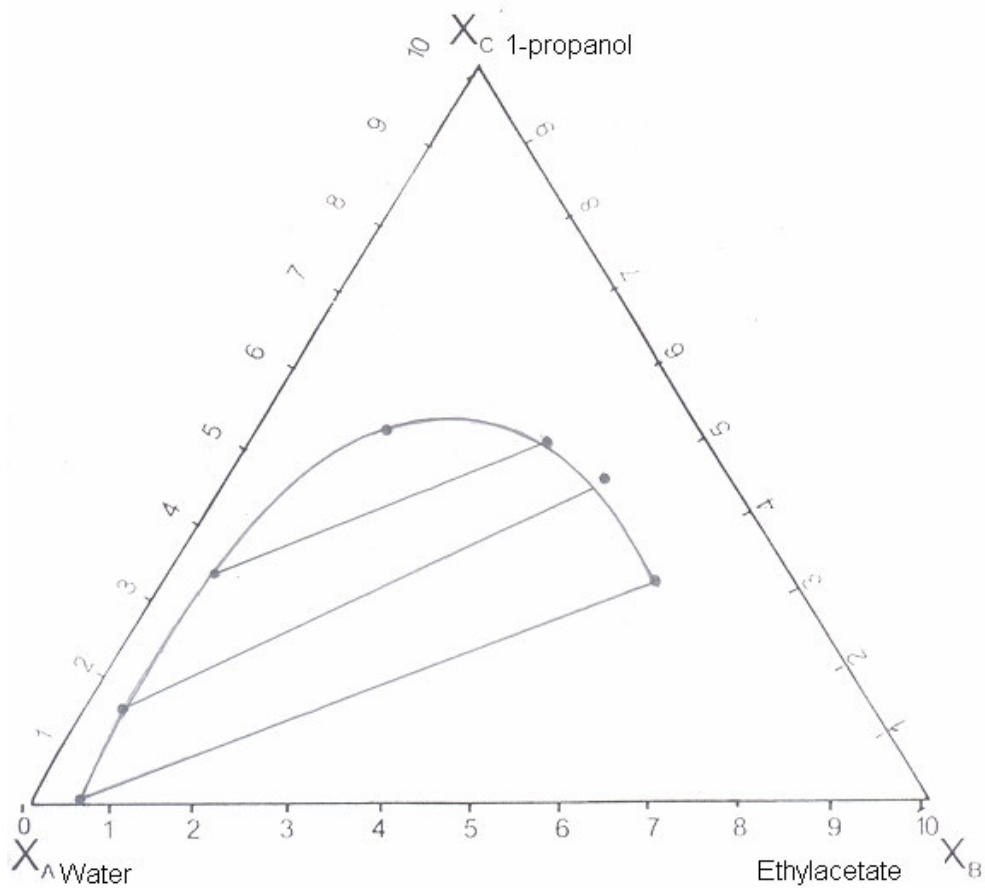
Fig. 42 Solubility Curve for 15% $(NH_4)_2SO_4$ (37ºC)
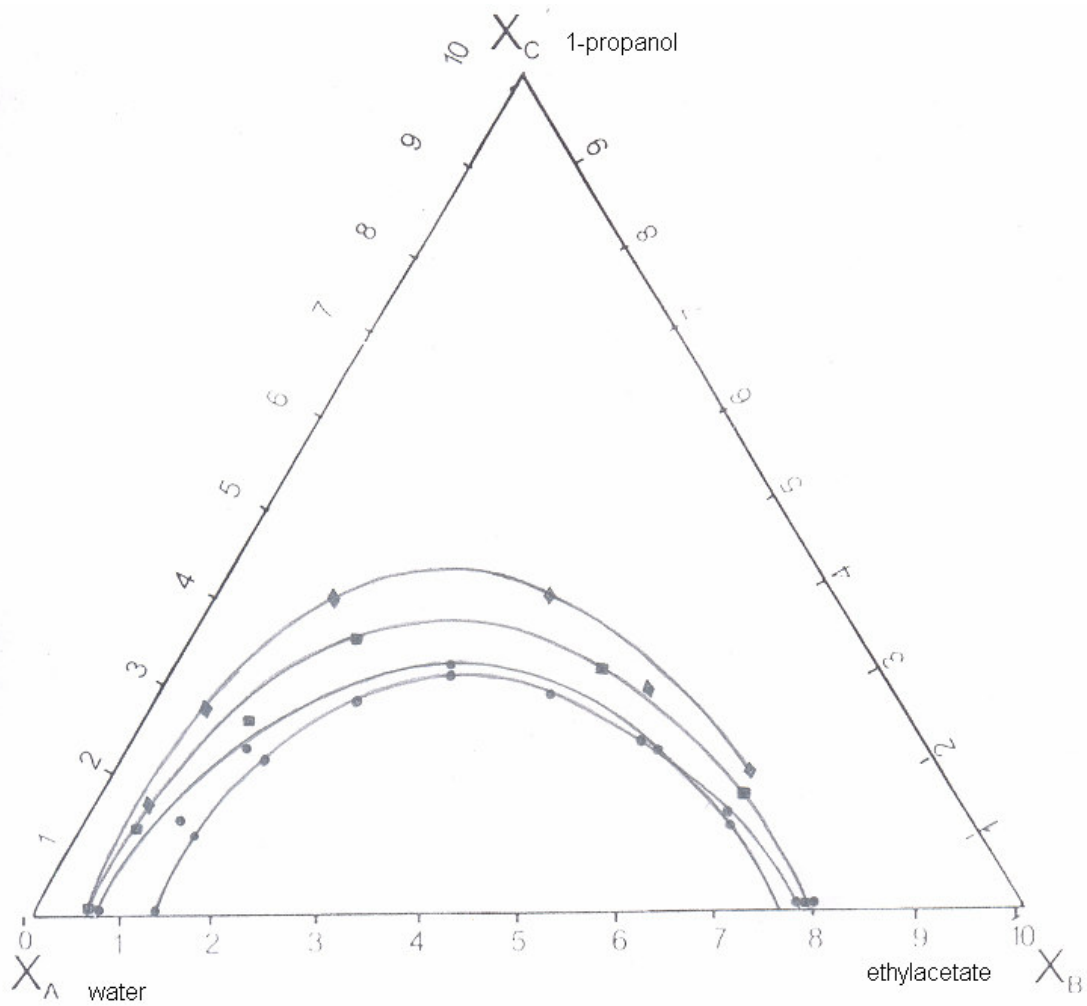
Fig. 43 Solubility Curve at 27ºC

•	No Salt
•	5% NaCl
▪	10% NaCl
♦	15% NaCl
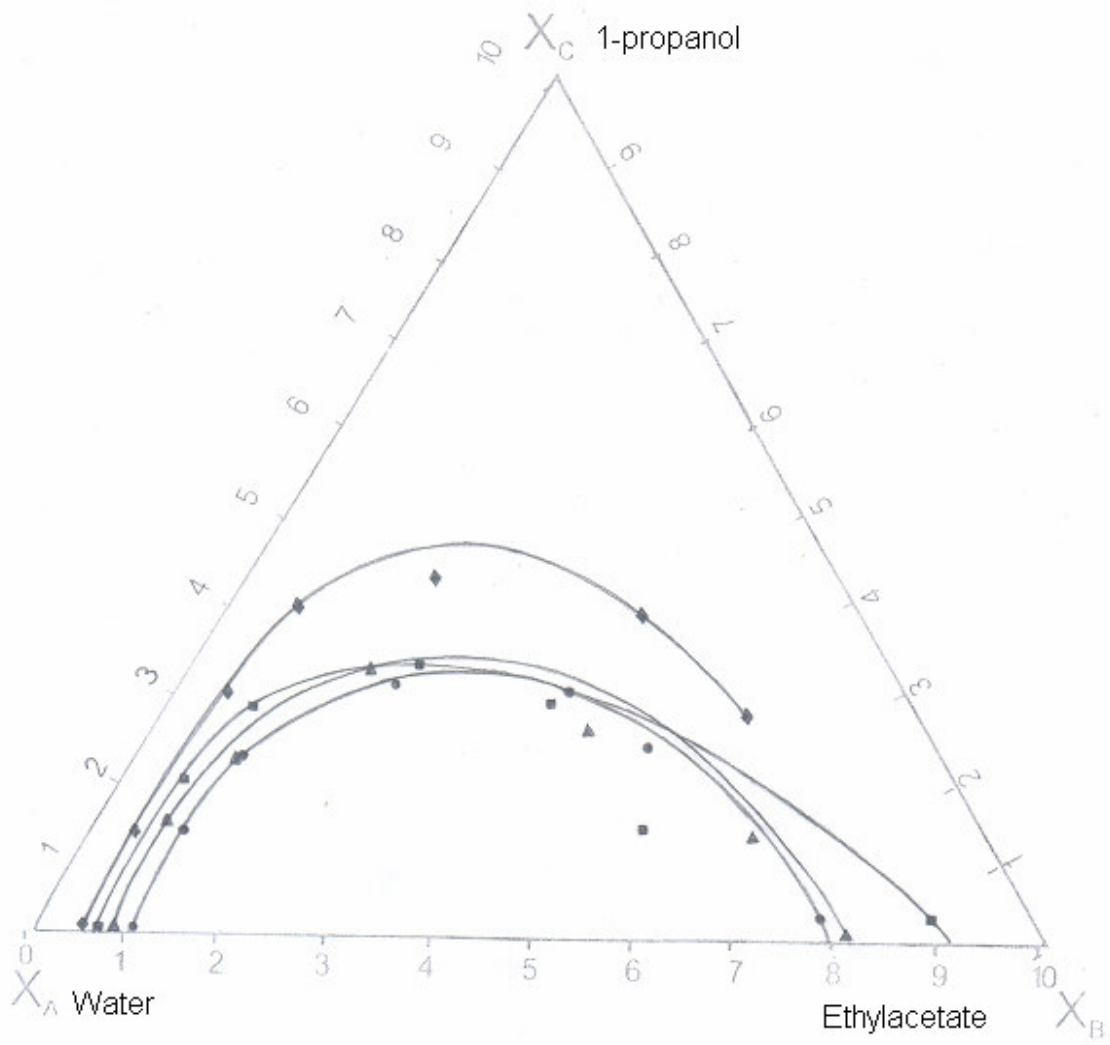
Fig. 44 Solubility Curve at 32ºC

- • No Salt
- ∇ 5% NaCl
- ▪ 10% NaCl
- ♦ 15% NaCl
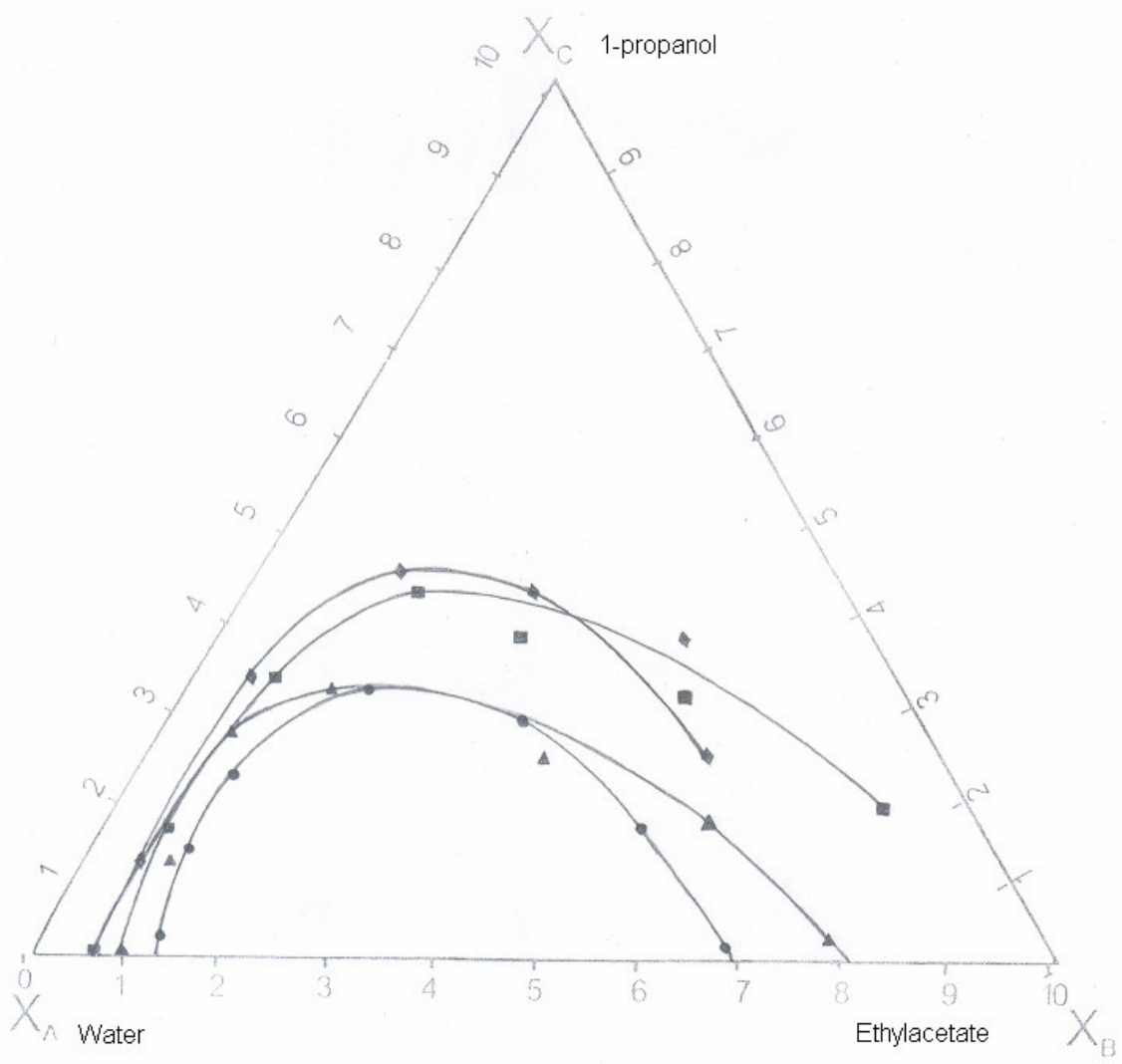
Fig. 45 Solubility Curve at 37ºC

- • No Salt
- ∇ 5% NaCl
- ▪ 10% NaCl
- ♦ 15% NaCl
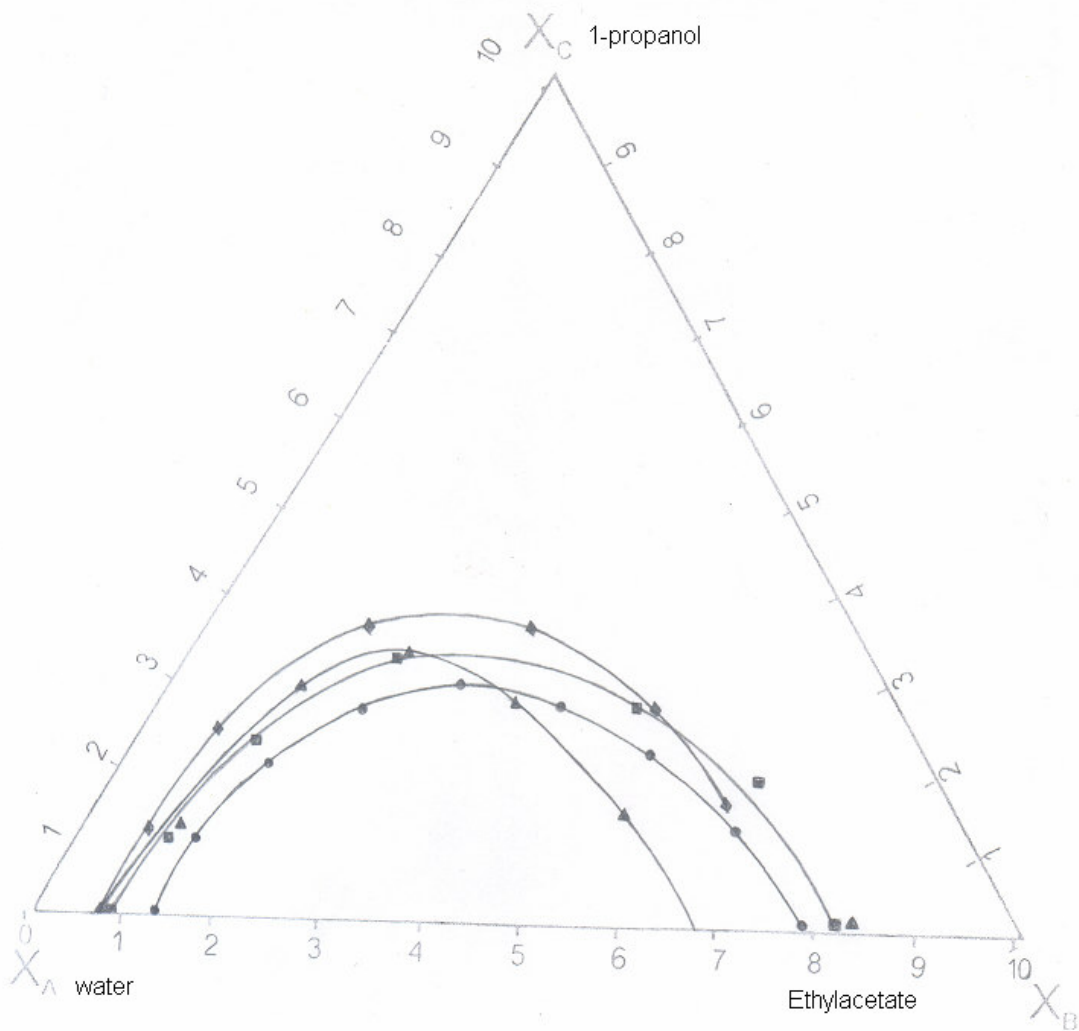
Fig. 46 Solubility Curve at 27ºC

- No Salt
∇ 5% $(NH_4)_2SO_4$
■ 10% $(NH_4)_2SO_4$
♦ 15% $(NH_4)_2SO_4$
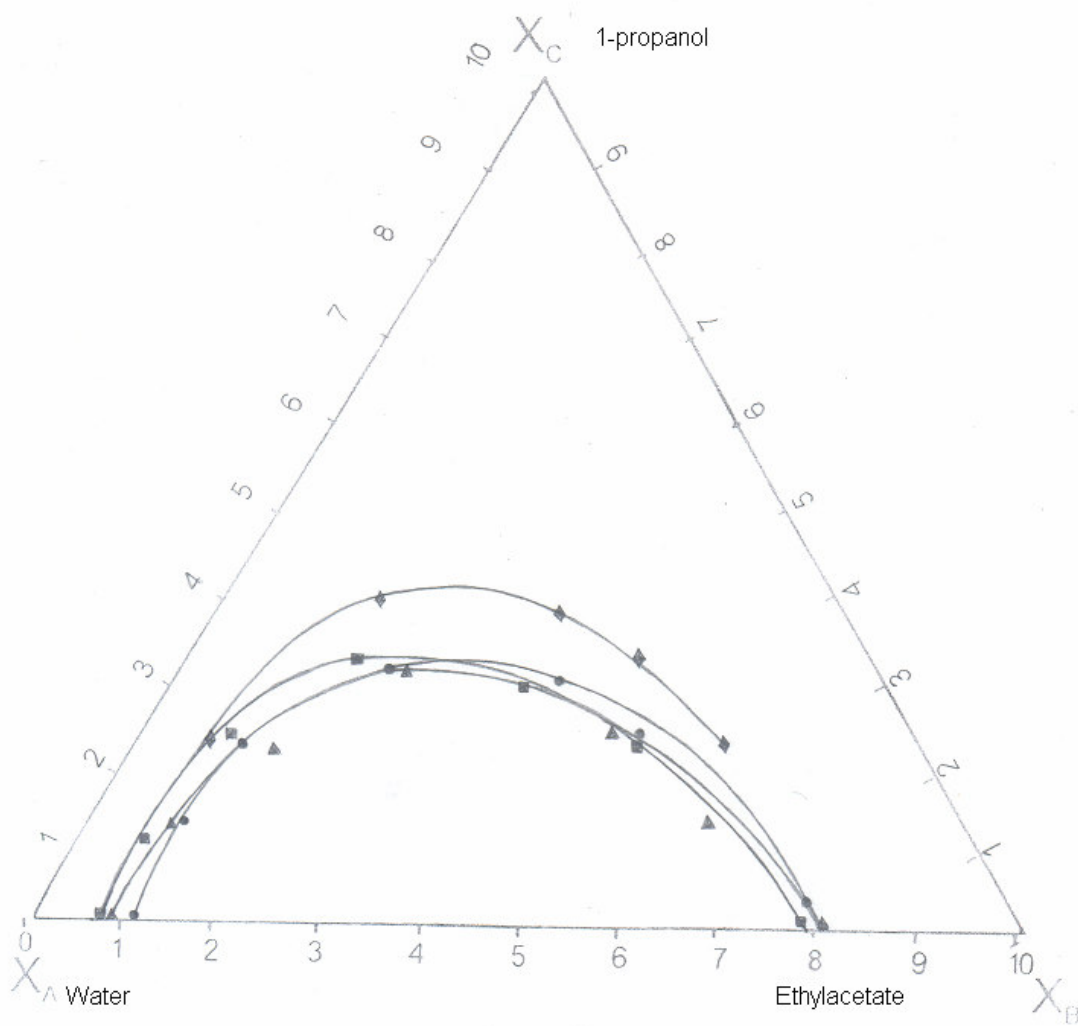
Fig. 47 Solubility Curve at 32ºC

- • No Salt
- ∇ 5% $(NH_4)_2SO_4$
- ▪ 10% $(NH_4)_2SO_4$
- ♦ 15% $(NH_4)_2SO_4$
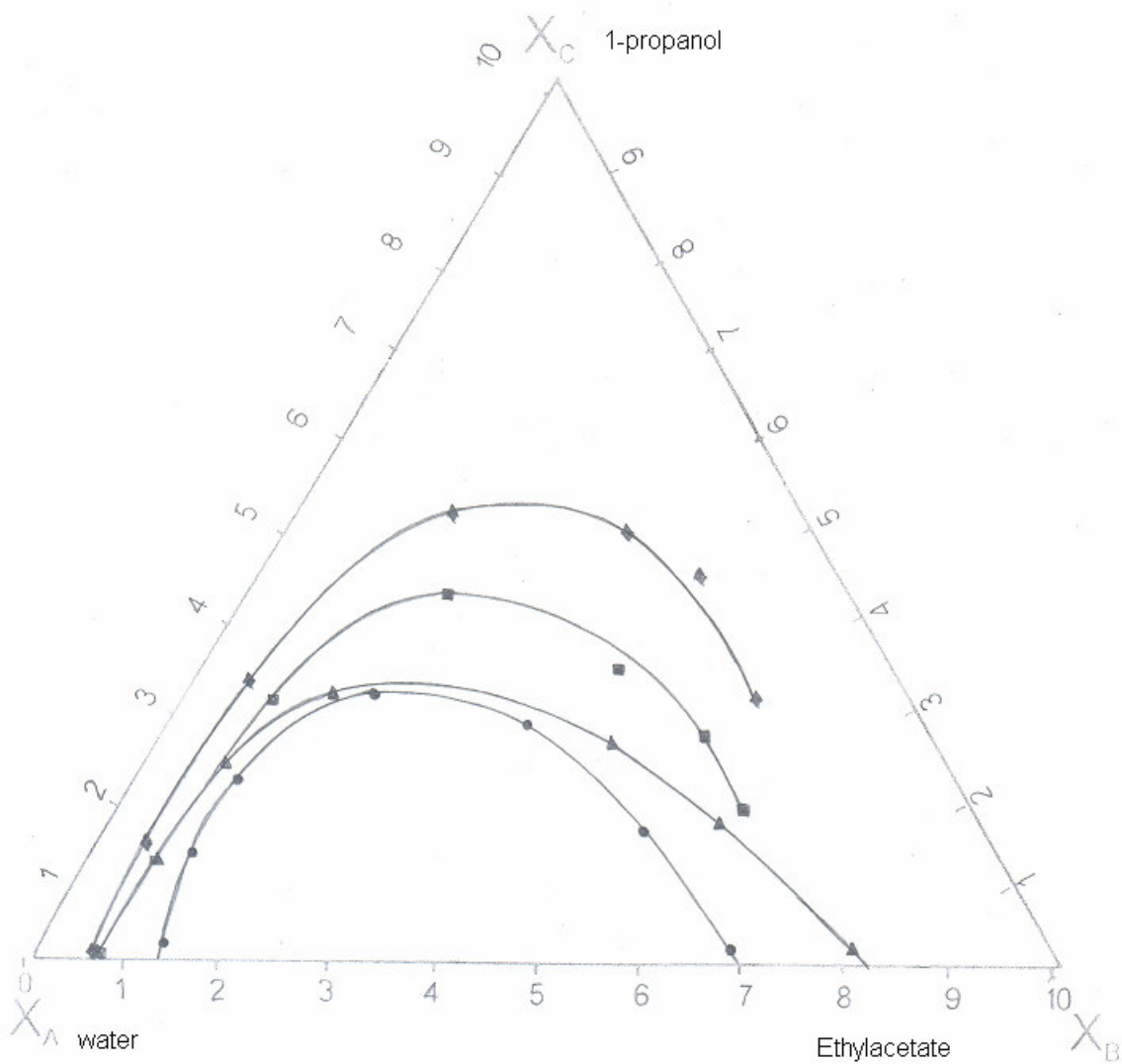
Fig. 48 Solubility Curve at 37ºC

- No Salt
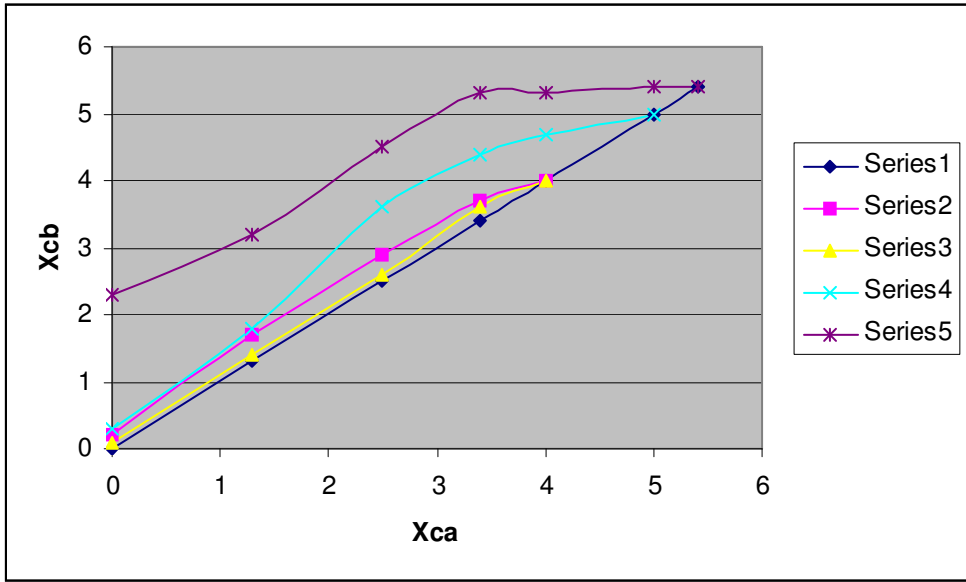∇ 5% $(NH_4)_2SO_4$
▪ 10% $(NH_4)_2SO_4$
♦ 15% $(NH_4)_2SO_4$

Fig.49 Distribution Curve at 27ºC

Series2-----No Salt(27°C)
Series3-----5% NaCl (27°C)
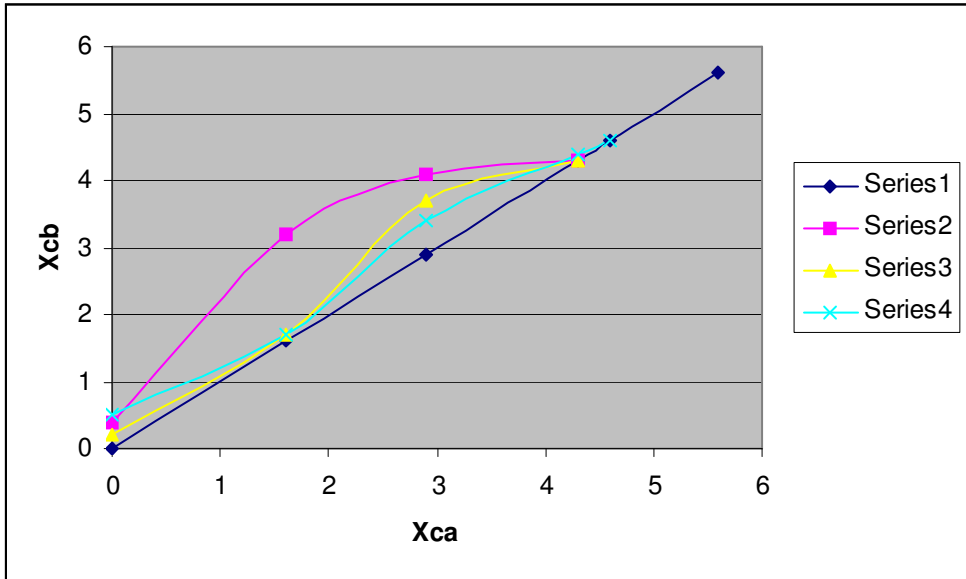Series4-----10% NaCl (27°C)
Series5-----15% NaCl (27°C)

Fig.50 Distribution Curve at 32ºC

Series2-----No Salt(32°C)
Series3-----5% NaCl (32°C)
Series4-----10% NaCl (32°C)
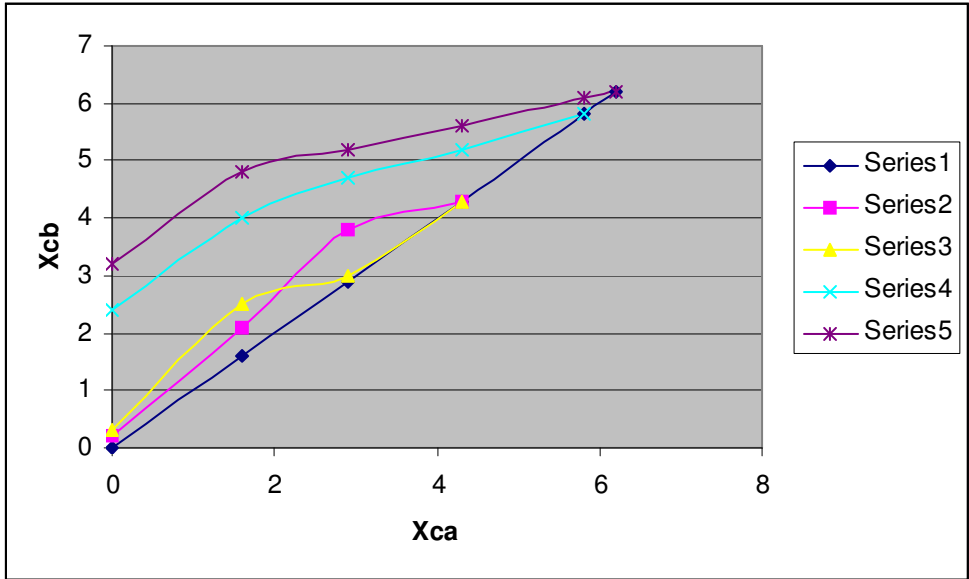Series5-----15% NaCl (32°C)

Fig.51 Distribution Curve at 37ºC

Series2-----No Salt(37°C)
Series3-----5% NaCl (37°C)
Series4-----10% NaCl (37°C)
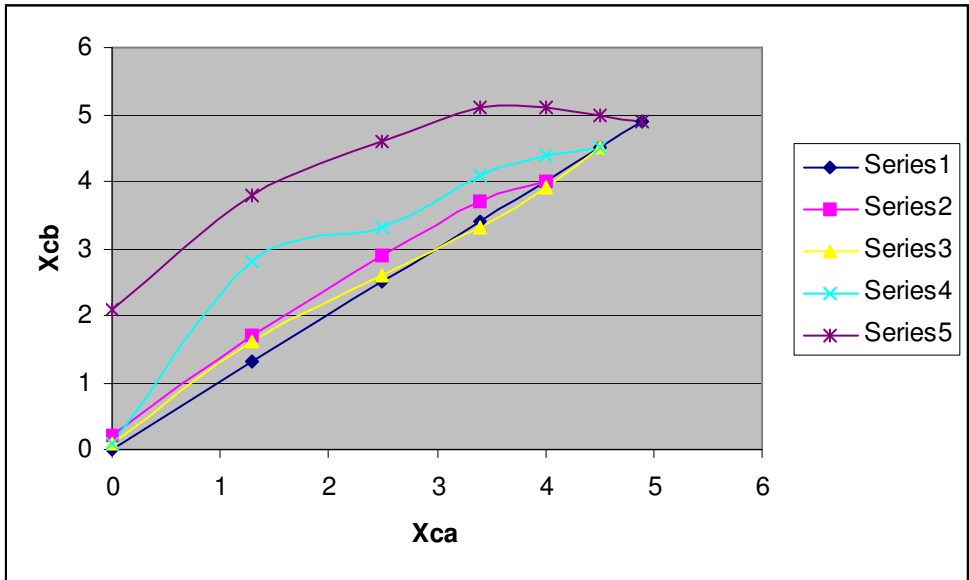Series5-----15% NaCl (37°C)

Fig.52 Distribution Curve at 27ºC

Series2-----No Salt(27°C)
Series3-----5% $(NH_4)_2SO_4$ (27°C)
Series4-----10% $(NH_4)_2SO_4$ (27°C)
Series5-----15% $(NH_4)_2SO_4$ (27°C)

Fig.53 Distribution Curve at 32ºC

Series2-----No Salt(32°C)
Series3-----5% $(NH_4)_2SO_4$ (32°C)
Series4-----10% $(NH_4)_2SO_4$ (32°C)
Series5-----15% $(NH_4)_2SO_4$ (32°C)
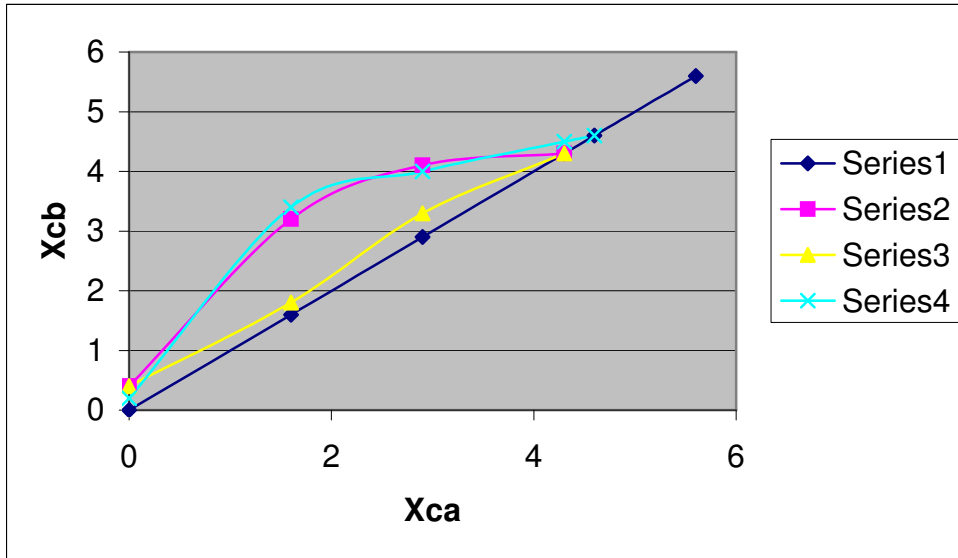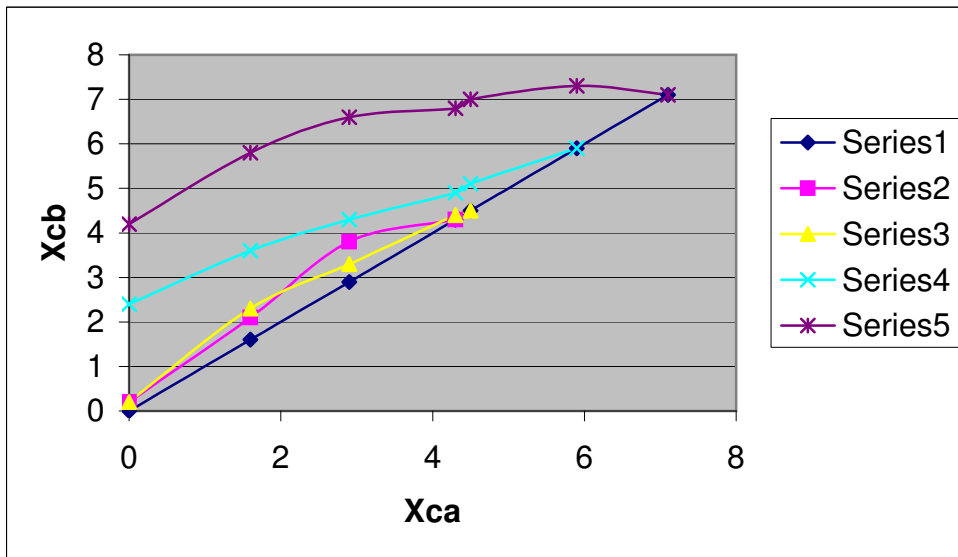

Fig.54 Distribution Curve at 37ºC

Series2-----No Salt(37°C)
Series3-----5% $(NH_4)_2SO_4$ (37°C)
Series4-----10% $(NH_4)_2SO_4$ (37°C)
Series5-----15% $(NH_4)_2SO_4$ (37°C)

5.4 RESULTS AND DISCUSSION

The Liquid-liquid equilibrium for ternary system was studied at atmospheric pressure and temperature of 27ºC, 32ºC and 37ºC. The ternary solubility data and the tie-line data for no salt, NaCl and $(NH_4)_2SO_4$ at 5%, 10% and 15% concentrations for the system Water + 1-propanol + Ethyl Acetate were determined at the above temperatures. It can be seen from the diagrams that the addition of the salts shifts the distribution in favour of ethyl acetate layer especially at higher salt concentrations. The presence of the salt decreases the solubility of the system increasing the heterogeneous zone. Heterogeneous area is an important characteristic. In the present system, the areas of the solubility curves are more in case of salt addition than that of without salt. At increasing salt concentrations more 1-propanol is transferred to the ethyl acetate phase. This process is usually referred to as salting out and is caused by the fact that the presence of high amounts of hydrated ions reduces the availability of the water molecules in the aqueous phase to the salvation of other solvents. Presence of salts mainly increase the concentrations of 1-propanol in organic phase and hence enlargement of the two-phase region occurred. These effects increase with salt concentrations and are maximum at salt saturation.

From the solubility curve at 27ºC for 5%, 10%, 15% concentrations of NaCl, it is found that the heterogeneous area is more for the 10% NaCl and the saturation level is obtained. Similarly considering the solubility curve at 32ºC for 5%, 10%, 15% concentration of NaCl it is found that 10% concentration of NaCl is quite effective in extracting 1-propanol from aqueous phase to organic phase. Though at 5% concentration of NaCl at 37ºC is also effective but it is less than 10% concentration of NaCl. Thus using the salt NaCl it is found that at 10% concentration of NaCl the maximum shifting of 1-propanol from aqueous phase to organic phase takes place.

From the solubility curve at 27ºC for 5%, 10%, 15% concentrations of $(NH_4)_2SO_4$, it is found that the heterogeneous area is more for the 10% $(NH_4)_2SO_4$ and the saturation level is obtained. Similarly considering the solubility curve at 32ºC for 5%, 10%, 15% concentration of $(NH_4)_2SO_4$ it is found that 10% concentration of $(NH_4)_2SO_4$ is quite effective in extracting 1-propanol from aqueous phase to organic phase. Though at 5% concentration of $(NH_4)_2SO_4$ at 37ºC is also effective but it is less than 10% concentration of $(NH_4)_2SO_4$. Thus using the salt $(NH_4)_2SO_4$ it is found that at 10% concentration of $(NH_4)_2SO_4$ the maximum shifting of 1-propanol from aqueous phase to organic phase takes place.

CHAPTER-6

CONCLUSION

6.1 CONCLUSION

The equilibrium diagram for ternary system Water + 1-Propanol + Ethyl acetate was determined at 27ºC, 32ºC and 37ºC. The effect of addition of salts like NaCl and $(NH_4)_2SO_4$ to the ternary system at different concentrations were studied at all these temperatures. The solubility data are tabulated in Table 5.1 and the equilibrium data are tabulated in Table 5.2. Considering these data the solubility curves and the distribution curves were plotted. All salt containing data are reported on salt free basis. The experimental tie-line data under no salt condition were determined and presented in respective tables. The experimental results lead to the conclusion that a salting out effect exists for all salts under study, increasing for higher salt concentrations. In conclusion it may be mentioned that concerted efforts on the investigations of the salt effect on the distribution of a solute between two partially miscible liquids have a potential scope for engineering applications.

The advantage of using solid inorganic salt in place of liquid separating agent in extraction processes is that by use of a small amount of solid salt bring about a substantial change in phase equilibrium in ternary liquid system. This fact is observed in case of ternary system under investigation. Thus it is concluded that this technique can be used effectively for extraction using a suitable solid salts.

6.2 FUTURE SCOPE OF WORK

These experimental data obtained further can be correlated with the different thermodynamic models like UNIQUAC (Universal quasi-chemical model), UNIFAC group contribution model, NRTL model etc. By correlating with these thermodynamic models the accuracy of the experimental data can be calculated.

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