“Separation of Acetonitrile + water Azeotropic mixture using Deep Eutectic Solvent as Entrainer by Extractive Distillation”

A thesis submitted to Thapar Institute of Engineering and Technology

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In

Chemistry

By

Shreya Sharma

(301702032)

SUPERVISOR

Dr. Neetu Singh

(Associate Professor)

Dr. Jai Prakash Kushwaha

(Associate Professor)

Department of Chemical Engineering

THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Department of Chemistry and Biochemistry

Thapar Institute of Engineering and Technology, Patiala 147004

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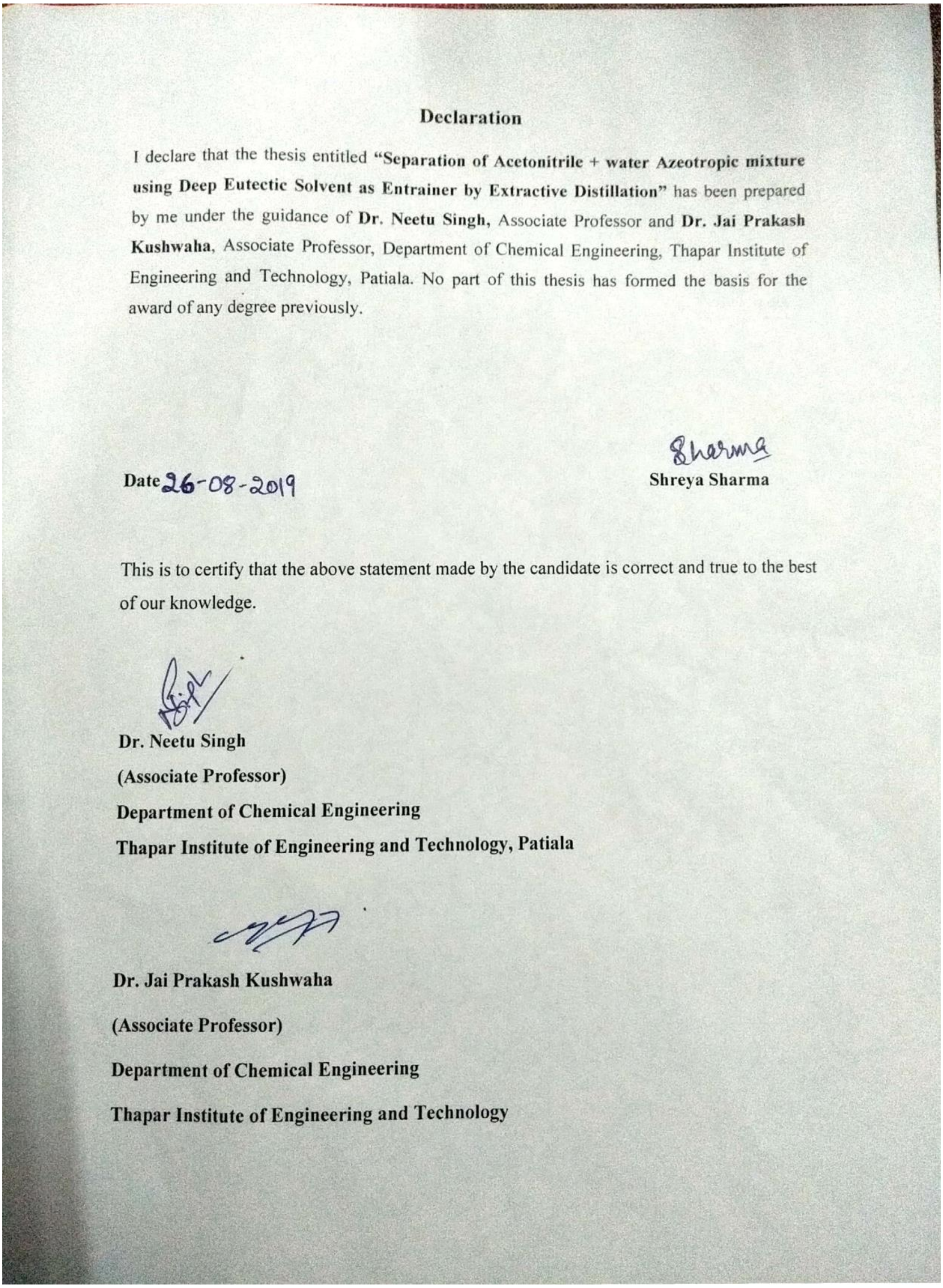


Declaration

I declare that the thesis entitled **"Separation of Acetonitrile + water Azeotropic mixture using Deep Eutectic Solvent as Entrainer by Extractive Distillation"** has been prepared by me under the guidance of **Dr. Neetu Singh,** Associate Professor and **Dr. Jai Prakash Kushwaha**, Associate Professor, Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala. No part of this thesis has formed the basis for the award of any degree previously.

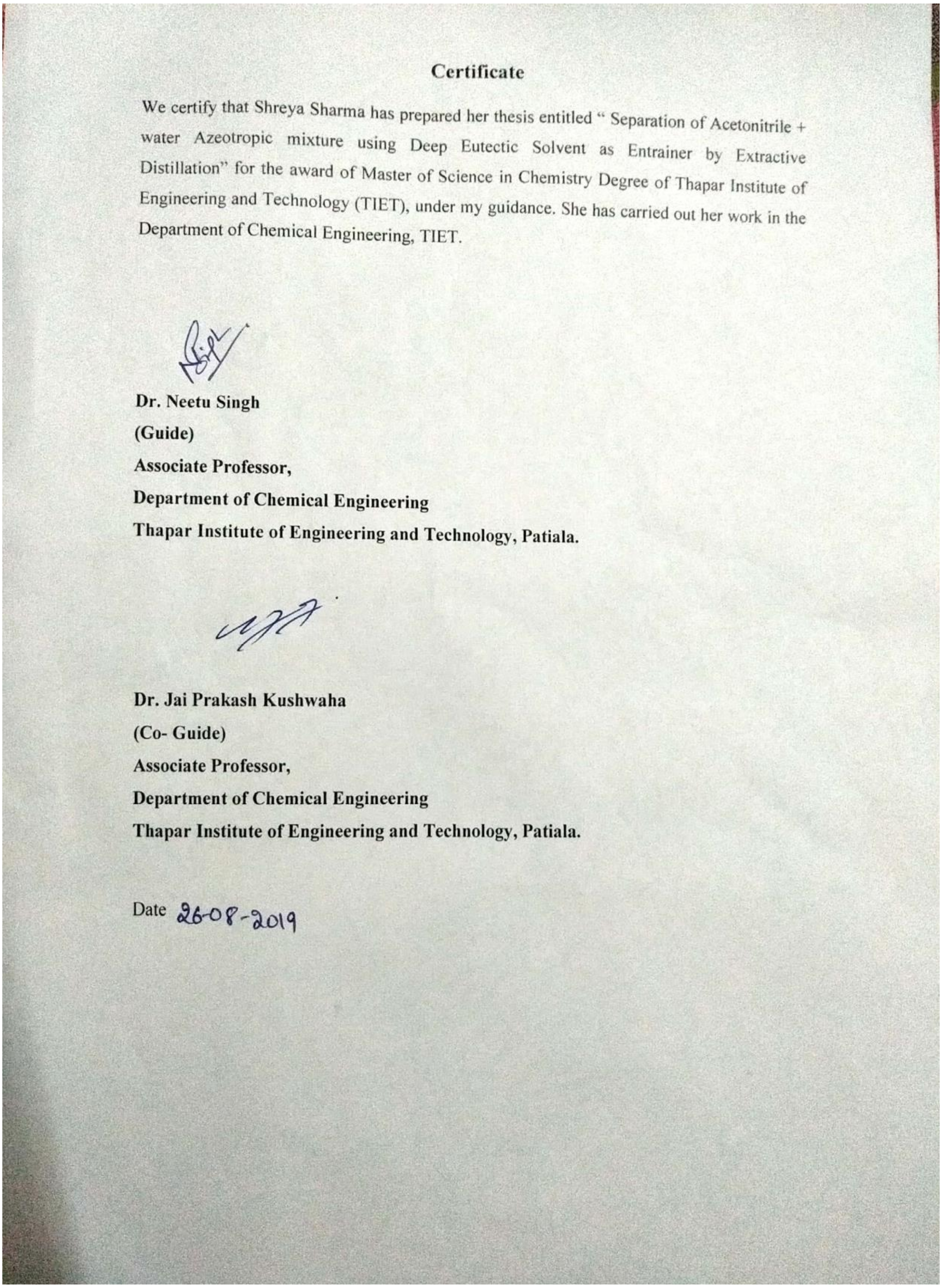
Sharma

Date 26-08-2019 **Shreya Sharma**

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

Dr. Neetu Singh
(Associate Professor)
Department of Chemical Engineering
Thapar Institute of Engineering and Technology, Patiala

Dr. Jai Prakash Kushwaha
(Associate Professor)
Department of Chemical Engineering
Thapar Institute of Engineering and Technology



Certificate

We certify that Shreya Sharma has prepared her thesis entitled " Separation of Acetonitrile + water Azeotropic mixture using Deep Eutectic Solvent as Entrainer by Extractive Distillation" for the award of Master of Science in Chemistry Degree of Thapar Institute of Engineering and Technology (TIET), under my guidance. She has carried out her work in the Department of Chemical Engineering, TIET.

Dr. Neetu Singh
(Guide)
Associate Professor,
Department of Chemical Engineering
Thapar Institute of Engineering and Technology, Patiala.

Dr. Jai Prakash Kushwaha
(Co- Guide)
Associate Professor,
Department of Chemical Engineering
Thapar Institute of Engineering and Technology, Patiala.

Date 26-08-2019

Acknowledgment

This thesis is a part of my journey in obtaining my post-graduation. I have not travelled in a vacuum in this journey. This thesis has been kept on tract and been seen through to completion with the support and encourage of numerous people. It is a pleasant task to express my thanks to those who contributed in many ways to the success of my study and made it an unforgettable for me.

To begin with, I bow with reverence, all humility and gratitude to thank the **Almighty** for his countless, gracious blessings showered on me.

I am privileged to express my deepest gratitude and heartfelt thanks to my esteemed teacher, learned guide and supervisor **Dr. Neetu Singh, Associate Professor, Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala**; who inculcated the values of dedication, diligence & discipline within me, without which I would not have seen this day. Her wise counsel & unflinching support throughout the preparation of this thesis has enabled me to achieve much more than I could have ever dreamt of. Thank you Mam, for guiding me.

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I would like to dedicate my thesis to my parents and my brother , to there countless efforts to motivate me at each and every step of my life and for showing trust in me and in my work.

Place: Patiala Regards,

Date: Shreya Sharma

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Abstract

Acetonitrile is an organic solvent which shows significant chemical and physical properties in the field of organic synthesis, pharmaceuticals, liquid chromatography. And also as a photosensitive material and extracting solvents. As it is a known toxic chemical, its ejection to water bodies is a serious threat, so there is a need of purification of acetonitrile from water because of its high importance.

Earlier, in industries, conventional and ionic solvents has been used for the separation but due to non-eco-friendly nature they had face some drawbacks. So researchers evolve green solvents which can reduce the solvent related damage green. Deep eutectic solvents (DESs) are now regarded as new emerging green solvents which are widely in use.

In this study, DES of ethylene glycol and choline chloride (EC) in ratio (2:1) acts as entrainer that separates the azeotropic blend of acetonitrile + water. A modified Othmer recirculation still was taken for quantifying the VLE data. For pseudo binary system DES EC(2:1) + water , DES EC(2:1) + ACN at room temperature the VLE data was calculated and for pseudo ternary system DES EC(2:1) + ACN + water the VLE data was computed at different DES mol % and these are- 5%, 10%, 12%. From this study, it has been found that EC (2:1) is a remarkable component that separates the ACN + water azeotropic blend. After this, a non-random NRTL model was used for thermodynamic modeling. Then, a fine confirmation of the experimental data and the forecast values for this system was found. In the result, it has been found that the used DES acts as a good entrainer for the separation ACN + water azeotrope.

CHAPTER 1 Introduction

Water is one of the chief chemical compound for all over earth, about 72% of the total earth's area is covered by water only. Because of its reckless usage and water body's pollution from decades we are now at the stage of facing water crisis. Water bodies are being polluted by agriculture, household things and majorly from industrial wastes. Industries are badly effecting our environment, discharging of wastewater from industries having high nutrient level (like nitrogen) and biological oxygen demand is highly affecting the water bodies, also with these, many chemical compounds are also responsible for the degradation of water bodies[1] and acetonitrile is one of them.

Acetonitrile (ACN) an organic nitrile with the formula CH_3CN is a liquid having ether like odor. It is polar and highly volatile solvent. It is obtained as a by-product from the manufacturing of acrylonitrile by ammoxidation of propylene[2].Aceonitrile is used in many ways, as, it is widely used as a chief solvent in pharmaceuticals[3], organic synthesis[4], as a photosensitive material[5], and in liquid chormatography[6]. It is also used in the removal of fatty acids from vegetable oils[7].Despite its usefulness it has some serious side effects as it is a toxic chemical. Long time inhalation of ACN can cause irritation of mucous membranes in humans, nausea, weakness[8-10], it can also cause dermatitis of skin[9]. The major problem of ACN which we are facing today is that it is highly miscible in water and this has been encountered in my chemical processes. It makes an Aziotropic mixture with water which is difficult to break so the separation of acetonitrile from water is necessary.

Azeotropes are the mixture of two or more liquids which has constant boiling point throughout the distillation. So there is a need of purification of acetonitrile from water as ACN-water mixture forms a minimum boiling azeotropes at (67.6 mol %) acetonitrile at 76.8 ℃ and standard atmospheric pressure[11]. Various methods have been reported previously in the literature like combined method of solvent extraction with butyl acetate and batch distillation,[12] extractive distillation with dimethylsulfoxide (DMSO),[13] pervaporation,[14-16] pressure-swing distillation,[17] adsorption,[18-19] and liquid-liquid extraction[20-21].Among them extractive distillation technique is mainly adapted by industries for the purification of azeotropic systems.

Extractive distillation is a technique in which separating agent (entrainer) are used, which basically interact with the components of the original mixture and then separate them out but selection of a successful entrainer is one of the most important concept as it is the one which decides the energy costs of the process. Previously, Ionic Liquids which is considered as a green solvents have been used by many researchers owing to there remarkable recycling, physical and chemical properties[22] but besides there potential efficiency and environmental friendly nature they have some serious limitations like toxicity, poor biodegradability, and high cost[23]. So to overcome these limitations another entrainer DES i.e. deep eutectic solvents also called as low transition temperature mixtures (LTTMs) are introduced.

DES is considered as a novel green solvent comprises quaternary salts and hydrogen bond donor at environmental temperature that has a low melting point from either of the two different components. They are now widely used in the extractive distillation technique because of there biodegradability, low cost and ease to prepare. They have also been used in many areas of chemistry like in electrochemistry, [24] enzyme reactions, [25] and organic synthesis[26-27] because of green properties and number of DESs available.

CHAPTER 2 Literature Review

Hadj-Kali et al (2017)[28] evaluated the liquid-liquid extraction of aziotropic mixture comprising n-heptane or n-octane, ethanol and n-hexane,(a binary aziotropic mixture) using DES. Conductor like Screening Model for Real Solvents method is applied on 10 DESs by assuming the activity coefficient at infinite dilution of ethanol and n-alkanes from where 3 DESs were selected for further experimental process where Tetrabutylammonium bromide/ Levulinic acid (TBAB/LA) of molar ratio 1:2 gives the best results. After this, ternary liquid-liquid extraction was also done on same DES. It was finally found that prediction by COSMO-RS of ternary tie-lines gave a remarkable results in its experimentation, having average RMSD value comes out to be 1.65%.

Devi et al (2017)[29] performed the heterogeneous azeotropic distillation for n-propanol-water system separation,n-propyl acetate acts entrainer. The outcomes then matched with different models like UNIFAC (VLE), UNIFAC (LLE) and some other thermodynamic models. A curve map (RCM) have been constructed from the above models for ternary system and the effect of n- propyl acetate in dissociation of mixture was also studied.

Peng et al (2017)[30] evaluated the separation of aziotropic mixture of ethanol- water by using DES ChCl/urea in (1:2) molar ratio as entrainer. The aziotropic point gets eliminated by adding ChCl/urea and further the non-random (NRTL) model for such system were measured and the assumed data was quite well to adjust in these system.

Liu et al (2017)[31] evaluated the separation of aqueous solution of isopropanol by liquid-liquid equilibrium (LLE) using isobutyl acetate, butyl acetate and butyl propionate as extractive solvents. The data's for ternary system and binary interactions were agreed by the NRTL and UNIQUAC models. From results, it was cleared that butyl propionate was an advantageous solvent for extraction as compared to other solvents.

Zhao et al (2017)[32] evaluated the extraction of lithium from its aqueous solution via experiments and COSMO-RS method. Firstly, anions were collected that has great affinity to lithium ion, for this a number of series of ionic liquids were made and then spectroscopically characterised by using NMR technique counting [P_{4444}]-based and [N_{4444}]-based ionic liquids having phosphate, phosphinate and long-chain carboxylic anions. From the extraction results, it has been cleared that Tetrabutylammonium mono-2-ethylhexyl(2-ethylhexyl)phosphate ([N_{4444}][EHPMEH]) has the highest efficiency for Li^+ extraction from its aqueous solution.

Further the extraction mechanism was scrutinized from slope analysis method and ATR-IR spectroscopy. He also proved that [N_{4444}][EHPMEH] can also separate the lithium ion form other alkali metals.

Zhang et al (2018)[33] evaluated the separation of aziotropic mixture of acetonitrile +methanol using ionic liquids as entrainer.1-butyl-3 methylimidazolium chloride ([BMIM][Cl]), 1-butyl-3 methylimidazolium bromide ([BMIM][Br]) and 1-butyl-3 methylimidazolium acetate ([BMIM][OAc] Imidazolium based ionic-liquids were used as entrainer. As a result, addition of entrainer built a salting-out effect on acetonitrile, therefore, there was a notable increase in the comparative volatility of ACN to methanol, the azeotropic point of acetonitrile + methanol gets break off when the ionic liquid reaches to a certain point. At last, the measured ternary vapor-liquid equilibrium (VLE) data was matched by NRTL model.

Jiang et al (2019)[34] evaluated the separation of allyl alcohol from its aqueous solution using two DESs, these are, ChCl/urea and ChCl/glycerine in 1:2 and 1:1 molar ratios respectively. The relative volatility was increased remarkably on the addition of DESs and ultimately, the aziotropic point breaks off. Finally, the vapor-liquid equilibrium (VLE) data as matched up by the non-random two-liquid NRTL model.

Shi et al (2013)[35] evaluated acetonitrile + ethyl acetate aziotropic mixture separation taking 1-octyl-3- methylimidazolium tetrafluoroborate ([OMIM]BF_4) as entrainer. Results proved the salt effect of the ionic liquid changes the relative volatility of the ethyl acetate to acetonitrile and break the aziotropic point when the ionic liquid reaches to mole fraction greater than 0.05 in liquid phase.

Sharma et al (2018)[36] performed the separation of acetonitrile + water via extractive distillation using choline chloride/ glycolic acid (GC) in (1:3 molar ratio) as entrainer. VLE data were calculated at different mole fractions and were then matched up with the non-random two-liquid NRTL model. Final results showed up that at certain content the LTTM i.e. GC (3:1) breaks off the aziotropic mixture of acetonitrile + water into there individual components.

Jain et el (2019)[37] evaluated the separation of isopropanol + water mixture by using 2, 2’,2”-Nitrilotrisethanol as entrainer. The VLE were calculated by using updated Othmer still. The experimental data for the ternary system (at 5mol%, 10mol% and 15mol% concentrations) proved that the comparative volatility of the isopropanol to water enhances on incorporation of triethanolamine and at certain content it will break off the azeotrope of isopropanol + water. Afterwards, more distantly the Non-Random Two Liquid model was taken under consideration to match up the experimental data, also, then thermodynamic equilibrium check was executed on the experimental data by employing the reformed McDermott-Ellis test and Wisnaik's L-W test.

Soukup et al (2014)[18] performed the separation of water from aqueous acetonitrile by adsorption process of water using silica-rooted stationary phases via normal-liquid phase chromatography. He explored the water adsorption on 16 silica-based stationary phases having different polarities. Among 16 stationary phases pentafluorophenylpropyl, octadecyl & cholesterol, phenyl, nitrile, hydrosilated matrices and organic silica were bonded on silica, Kal-fischer coulometric titrations and frontal analysis methods were applied for this investigation. In the results, notable connections were found among separating compound of strong polarity differences and water uptake.

Khayet et al (2008)[15] evaluated a separation technique under the name Pervaporation separation which was applied on aqueous solutions of acetonitrile, ethanol and acetone. Firstly, binary separation of water with all the three compounds was performed and then, the impact of feed temperature and feed concentration on Pervaporation staging was studied also, organic selectivity, total or partial permeability were taken into consideration. In the result, Pervaporation was applied to the water solution having acetone, acetonitrile and ethanol at 40℃ and after this process, the organic selectivity came out to be in the order of acetone>acetonitrile>ethanol.

Chaudhari et al (2018)[38] investigated Pervaporation separation of azeotropic mixture of acetonitrile + water by using high water empathy PVA-PVAm blended membrane. To develop blended membrane poly (vinyl alcohol) and poly (vinyl amine), hydrophobic polymers have been used and cross-linked. The agent used for crosslinking was glutaraldehyde. Different techniques were used for the characterisation of blended membrane before its application to Pervaporation separation. As a result, it has proved that the membrane behaves as a third phase to successfully break the azeotrope.

CHAPTER 3 Materials and Methods

3.1 Chemicals Used: - Acetonitrile of HPLC class with (minimum 99.8%) of purity was procured from Merck Life Science Chemicals, Choline chloride of (>98.0%) purity was procured by TCI chemicals, Ethylene glycol of (minimum 99%) purity was given by LOBA chemicals , distilled water was provided by our laboratory, the chemical's record is encapsulated in **(Table 1).** Being hygroscopic in nature choline chloride was first dried in the vacuum oven for 8-10 hours before preparation of DES. Kal-Fischer reagent was used to check the water traces in the prepared DES and bottom product.

Table 3.1. Chemicals taken.

Name	CAS No.	Source	Purity	Purification
Acetonitrile	75-05-8	Merck chemicals	≥99.8%	None
Ethylene glycol	107-21-1	LOBA chemicals	>98%	Vacuum drying
Choline chloride	67-48-1	TCI chemicals	>98%	Vacuum drying
Karl Fischer reagent	7446-09-5	Merck chemicals	>99%	None
Double distilled water		Our laboratory		

3.2 Preparation of DES (EC2:1) and Characterisation: -

Ethylene glycol and choline chloride were collectively placed in a 50 mL conical flask in 2:1 molar ratios respectively. An electronic balance of ±0.0001 g precision was used for measuring the weight of respective chemicals. After addition to the conical flask, both were mixed homogenously for about half an hour and then constant heating was supplied by putting the conical flask in thermostatic oil bath which was managed at temperature 80-85℃ (±0.1℃). The mixture was stirred till the contents get completely converted to white, clear solution then, heat supply was turned off, let the solution cool down at environmental temperature. Now, density and molecular weight of the prepared DES was evaluated. The density was measured using picnometer. The evaluated density and molecular weight comes out to be 1262 kg/m^3 and 87.921g/mol respectively. The hydrogen bonding between ethylene glycol & ChCl is represented in **Figure 3.1**. Prepared DES 2:1 was also characterised by Fourier Transform-Infrared spectroscopy who's spectra is visible in **Figure 3.2**.

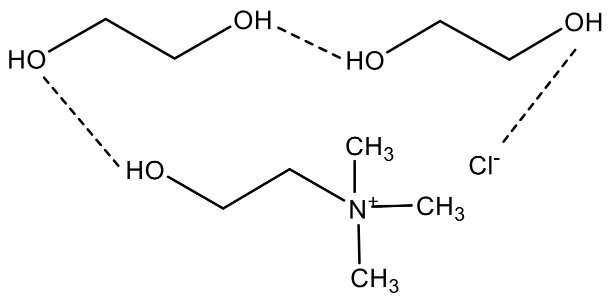


Figure 3.1. Mechanism of H-Bonding in EC2:1

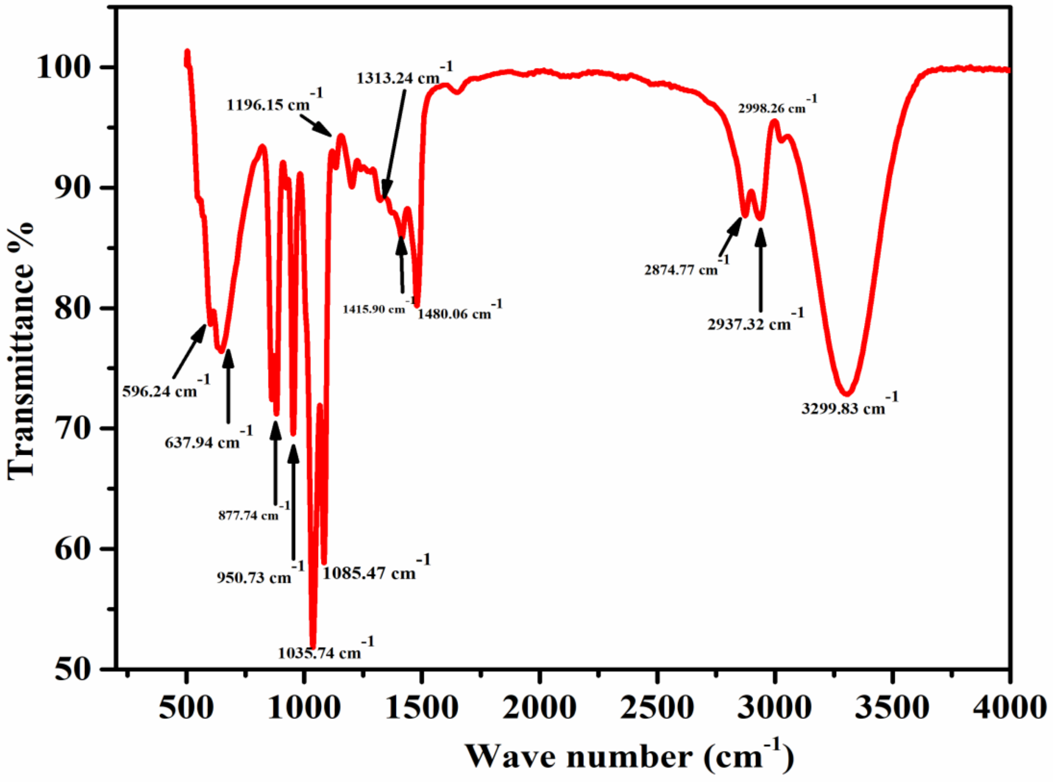


Figure 3.2. FTIR spectrum of EC (2:1) pure DES

3.3 Apparatus used and Procedure:

For the analysis of vapor-liquid equilibrium (VLE) data, a modified Othmer recirculation still (shown in **Figure 3.2.**)[36] is used consisting of a boiling still of (150 mL approximately) who has a wire heater of nichrome which delivers to boil the mixture. This wire heater is sealed by the glass. A magnetic stirrer was taken for stirring the contents of the boiling still. The boiling still has two-side openings: the left one to raffle the liquid sample and to lodge the thermometer and the right one to collect condensate recover. Vapor produced inside still drive through an air-cooled condenser where another thermometer is taken in. The partially condensed vapor and condensate move to another condenser which is cooled by water, and then it moves down from this water cooled condenser to the condensate bulb that is further in connection with sampling port where condensate collects. Nearly, every vapor condenses in the recirculation condenser and if any partially condensed vapors remain, they will experience condensation in separate water-cooled condenser. A precise thermometer of 0.1 K was taken to measure the equilibrium temperature and in order to supply electricity to the wire heater, an autotransformer was used.

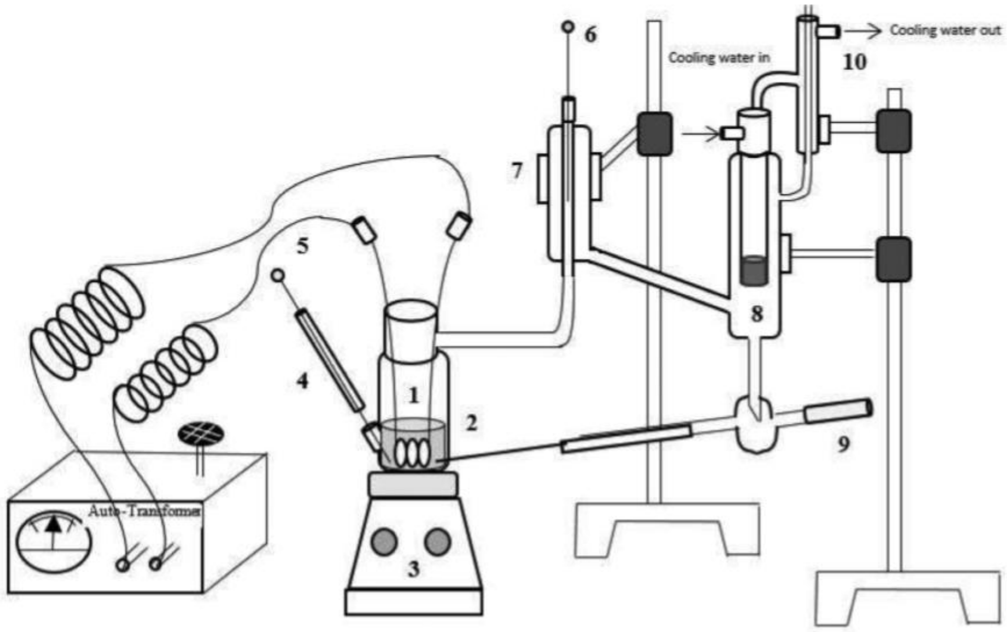


Figure 3.2. Schematic depiction of updated Othmer recirculation still, comprising of 1- the boiling still; 2- heating mantle; 3- magnetic stirrer; 4- liquid phase sampling port; 5 & 6- thermometers; 7- air cooled condenser; 8- water-cooled recirculation condenser; 9- condensate sampling port; 10- water cooled condenser).

3.4 Composition Analysis

To direct the equilibrium acetonitrile compositions in condensed vapor phase, Gas chromatographer furnished with Flame ionisation detector (FID) was taken into consideration. GC method is tabulated in **(Table 2)**. A Thermo Scientific TG- Bond Q column was used which act as a media for separation.

Table 3.2. Conditions for GC considered for vapor and liquid phase analysis.

Type Of Detector	FID Detector
Column type	TG-Bond Q (30 m; 0.53 mm; 20.0 µm)
Temperature Detector	250˚C
Injector temperature	200˚C
Injection volume	1.0 µL
Carrier gas	Helium
Flow rate	5.0 mL min^{-1} (unchanged)

No detection of DES was there in vapor phase. 180℃ temperature of oven was maintained. This same procedure was then applied to check the acetonitrile compositions in liquid phase. During entry I the column the DES was trapped as it is liquid in nature and for this the Glass Liners were used for this. The amount of concentration was recognised through mass balance to calculate make-ups of vapor phases and liquid phases in mole fractions.

Chapter 4 Results & Discussions

4.1 Effectiveness of EC2:1 as Extracting Agent

As it is important to illustrate the effectiveness of EC2:1 for separating the ACN−water azeotrope, so VLE experiments have been performed regarding azeotropic blend of ACN−water in the presence of EC2:1. The relative volatility(α_{12}) for the ACN + water is unity at the azeotropic point, so to break this point the relative volatility should be higher than unity.The influence of entrainer concentration on comparative volatility (α_{12}) of azeotropic blend of ACN−water was analysed by changing the EC2:1 composition from 0−15 mol% at 101.3 kPa. **Table 4.1** and **Figure 4.1** represents the influence of EC2:1 amount on α_{12} of azeotropic blend of ACN−water (67.4 mol % ACN). It can be noticed from **Figure 4.1** that with the incorporation of EC2:1, the comparative volatilities of ACN to water gets better and the consequence is more evident on increase in EC2:1 concentration. At 15 mol % the relative volatility $\alpha_{12} = 3.28$ and this value is 3.2 times higher thn free EC (2:1) system.

Table 4.1. Effect of EC2:1 concentration on comparative volatility α_{12} ($x_1' \approx 0.674$) of ACN (1) + water (2) system, comparative volatilities α_{12} at atmospheric pressure (101.32 kPa): EC2:1= (0 to 15) mol%.

Mol% of EC2:1	Relative volatility (α_{12})
0.0	1.06
2.0	1.29
5.0	1.6
7.0	1.86
10.0	2.18
12.0	2.49
15.0	3.28

Standard uncertainty $mol\%\ of\ EC$ (2: 1)= 0.1, $u(\alpha) = 0.025$.

4.2 Vapor- Liquid Equilibrium Data

4.2.1 Pseudobinary Vapor- Liquid Equilibrium Data

The isobaric VLE data for the pseudobinary system of water(1) + EC 2:1 (2); ACN(1) + EC2:1 (2) were calculated at 101.32 kPa. The experimental data are revealed in **Table 4.2** and depicted in **Figure 4.2** which shows the increase in T_b of water and acetonitrile on incorporation of DES EC (2:1). After incorporation of DES the temperature of both water and acetonitrile was high.

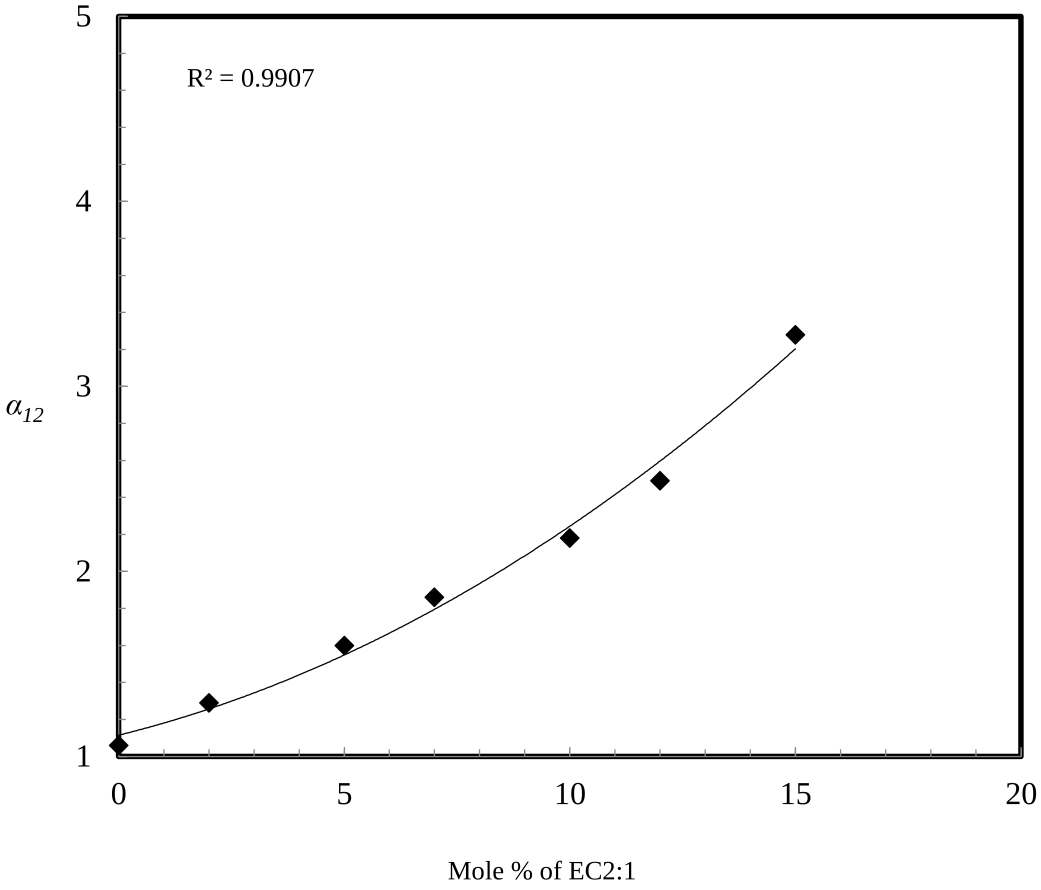


Figure 4.1. Effect of EC2:1 concentration on comparative volatility α_{12} ($x_1^{'} \approx 0.675$) of the of ACN (1) + water (2) system at 101.3 kPa.

4.2.2 Pseudoternary Vapor- Liquid Equilibrium Data

The VLE data for pseudoternary system of ACN(1) + water (2) + EC 2:1 (3) were generated experimentally at 101.32 kPa. Different DES concentrations (5%, 10%, 12% mol/mol)were selected for this study based on previous experimentations. The resulted data for all the three mol percents (5%, 10%, 12%) is encapsulated in **Table 4.3** in which x_1 represents the mole fraction of ACN (liquid phase) and x_1' represents the mole fraction of ACN (liquid phase) on DES free basis, y_1 represents the mole fraction of ACN (gaseous phase) and “T” represents the equilibrium temperature. To illustrate the salting-out effect originated by the incorporation of DES (EC 2:1) at mole fractions (0.05, 0.1 and 0.12), the temperature vs compositions diagrams are shown in **Figure 4.3 (a), (b)** and **(c)**.

Table 4.2. Experimental VLE data and correlated results of pseudobinary subsystems, Activity Coefficient γ_i, deviation in activity Coefficient $\Delta\gamma_i$ and deviation in equilibrium temperature ΔT at 101.32 kPa.

Water (1) + EC (2:1, mol/mol) (2)

S.No.	$T\,(K)$	Mole % of EC (2:1)	x_1	$\gamma_1^{\exp}$	$\Delta\gamma_1^{a}$	$\Delta T^{b}\,(K)$
1	373.1	0.00	1.000	1.002	0.002	0.00
2	373.2	1.19	0.995	1.003	0.003	0.03
3	373.5	2.48	0.979	1.008	0.006	0.11
4	373.9	3.88	0.966	1.007	0.002	-0.01
5	374.5	5.41	0.927	1.027	0.006	0.11
6	375.0	7.09	0.893	1.047	0.005	0.08
7	375.7	8.93	0.826	1.104	0.007	0.13
8	376.5	10.97	0.746	1.189	0.010	0.19
9	377.4	13.24	0.705	1.218	-0.007	-0.21
10	378.5	15.77	0.640	1.291	-0.009	-0.24
11	379.2	18.62	0.601	1.341	-0.005	-0.15
12	380.2	21.85	0.561	1.387	-0.004	-0.14
13	381.5	25.55	0.513	1.451	0.005	0.04
14	383.2	29.82	0.467	1.503	0.006	0.07
15	385.1	34.81	0.428	1.539	0.000	-0.04

ACN (1) + EC (2:1, mol/mol) (2)

S.No.	$T\,(K)$	Mole % of EC (2:1)	x_1	$\gamma_1^{\exp}$	$\Delta\gamma_1^{a}$	ΔT^{b} (K)
1	354.7	0.00	1.000	0.999	-0.001	0.07
2	355.0	3.41	0.983	1.006	0.005	-0.11
3	355.5	6.94	0.963	1.011	0.006	-0.13
4	356.3	10.59	0.918	1.035	0.009	-0.24
5	357.2	14.37	0.856	1.080	0.009	-0.21
6	358.3	18.29	0.762	1.174	0.006	-0.11
7	359.2	22.35	0.688	1.265	0.006	-0.10
8	360.4	26.56	0.636	1.320	-0.008	0.26
9	362.0	30.92	0.562	1.424	-0.007	0.21
10	364.0	35.46	0.496	1.520	-0.005	0.17
11	366.2	40.17	0.443	1.596	-0.004	0.14
12	368.5	45.08	0.396	1.671	0.005	-0.05
13	371.0	50.18	0.359	1.715	-0.002	0.08
14	374.0	55.50	0.318	1.781	0.008	-0.12

Standard uncertainty $u(x_1) = 0.003, u(T) = 0.1\ K, u(mol\%\ of\ EC2{:}1) = 0.1, u(P) = 0.05\ kPa.$

a $\Delta\gamma_1 = \gamma_1^{\exp} - \gamma_1^{cal}$, **b** $\Delta T = T^{\exp} - T^{cal}$

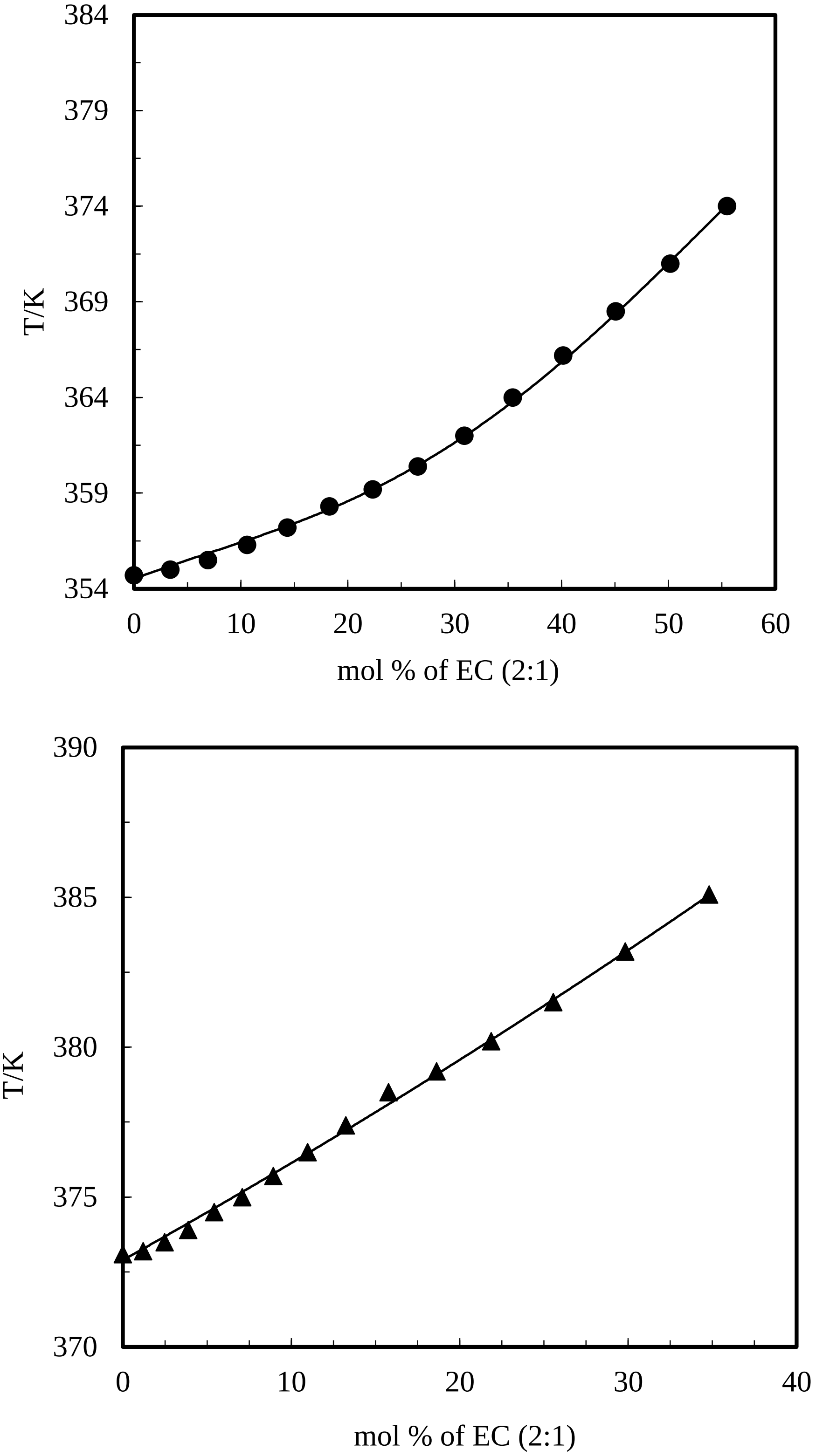


Figure 4.2. Effect of EC2:1 on the normal boiling point of ACN and water at 101.32 kPa. Symbols: experimental data for ACN (●) and water (▲). Solid lines: calculations based on the NRTL model.

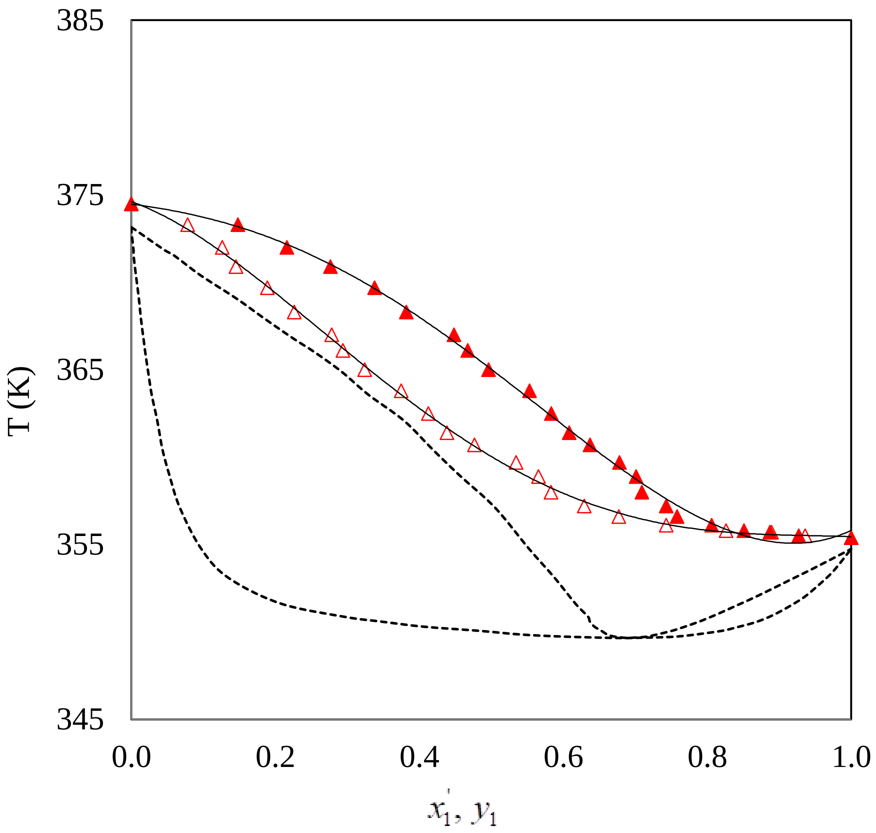
Table 4.3. Experimental Isobaric VLE data for ACN(1) + water(2) + EC1:1 (3) system, experimental Activity Coefficient $\gamma_i^{exp}$and Relative Volatilities α_{12} at 101.32 kPa. Presence of EC2: 1 was not detected in the vapor phase.

S.No.	T (K)	$x_1^{'}$	x_1	x_2	y_1	γ_1^{exp}	γ_2^{exp}	α_{12}
Ethylene glycol/Choline Chloride 2:1= 5 mol%								
1	355.4	1.000			1.000			
2	355.5	0.936	0.795	0.155	0.927	1.137	0.916	0.80
3	355.7	0.889	0.776	0.174	0.887	1.108	1.255	0.89
4	355.8	0.826	0.722	0.228	0.851	1.138	1.261	1.07
5	356.1	0.743	0.673	0.278	0.806	1.147	1.327	1.32
6	356.6	0.677	0.633	0.319	0.758	1.128	1.418	1.40
7	357.2	0.629	0.597	0.354	0.743	1.153	1.322	1.61
8	358.0	0.583	0.550	0.399	0.709	1.164	1.289	1.67
9	358.9	0.565	0.531	0.419	0.701	1.159	1.218	1.64
10	359.7	0.534	0.498	0.451	0.678	1.169	1.179	1.65
11	360.7	0.476	0.462	0.487	0.637	1.149	1.184	1.77
12	361.4	0.438	0.415	0.533	0.608	1.196	1.137	1.81
13	362.5	0.413	0.391	0.559	0.583	1.178	1.106	1.70
14	363.8	0.375	0.347	0.602	0.553	1.211	1.048	1.74
15	365.0	0.324	0.295	0.656	0.496	1.232	1.037	1.86
16	366.1	0.294	0.269	0.681	0.467	1.231	1.014	1.72
17	367.0	0.278	0.252	0.699	0.448	1.229	0.989	1.59
18	368.3	0.226	0.205	0.745	0.382	1.241	0.990	1.53
19	369.7	0.189	0.170	0.780	0.338	1.271	0.962	1.40
20	370.9	0.145	0.140	0.808	0.276	1.221	0.971	1.20
21	372.0	0.126	0.106	0.844	0.216	1.220	0.968	1.91
22	373.3	0.078	0.072	0.878	0.148	1.195	0.965	2.05
23	374.5	0.000			0.000			
Ethylene glycol/Choline Chloride 2:1= 10 mol%								
1	356.2	1.000			1.000			
2	356.4	0.891	0.799	0.101	0.929	1.103	1.327	1.59
3	356.7	0.862	0.774	0.126	0.901	1.095	1.455	1.46
4	357.0	0.834	0.749	0.152	0.887	1.103	1.365	1.56
5	357.5	0.779	0.710	0.190	0.868	1.121	1.250	1.87
6	357.9	0.742	0.662	0.238	0.842	1.153	1.174	1.86
7	358.4	0.705	0.631	0.269	0.827	1.169	1.120	2.00
8	359.1	0.639	0.578	0.324	0.780	1.180	1.147	2.00
9	359.7	0.601	0.542	0.359	0.747	1.183	1.164	1.96
10	360.5	0.576	0.522	0.381	0.740	1.188	1.092	2.10
11	361.5	0.521	0.472	0.428	0.685	1.180	1.134	2.00
12	362.4	0.469	0.427	0.473	0.659	1.222	1.074	2.19
13	363.2	0.426	0.386	0.515	0.634	1.269	1.027	2.33

14	364.3	0.403	0.359	0.545	0.605	1.262	1.005	2.27
15	365.5	0.385	0.339	0.561	0.586	1.252	0.976	2.26
16	366.4	0.315	0.285	0.615	0.529	1.308	0.980	2.44
17	367.7	0.261	0.238	0.663	0.469	1.336	0.977	2.50
18	368.9	0.234	0.213	0.688	0.428	1.316	0.970	2.45
19	370.3	0.217	0.199	0.711	0.409	1.296	0.921	2.50
20	371.6	0.179	0.161	0.739	0.345	1.300	0.937	2.41
21	373.1	0.153	0.135	0.766	0.311	1.340	0.901	2.50
22	374.7	0.116	0.098	0.802	0.239	1.352	0.898	2.39
23	376.2	0.000			0.000			
Ethylene glycol/Choline Chloride 2:1= 12 mol%								
1	356.5	1.000			1.000			
2	356.5	0.935	0.789	0.091	0.977	1.171	0.472	2.95
3	356.7	0.902	0.762	0.119	0.955	1.177	0.712	2.27
4	357.1	0.852	0.720	0.160	0.935	1.205	0.745	2.50
5	357.4	0.827	0.701	0.180	0.921	1.209	0.793	2.43
6	357.9	0.754	0.618	0.264	0.863	1.265	0.920	2.06
7	358.5	0.678	0.567	0.313	0.821	1.289	0.989	2.18
8	359.3	0.627	0.516	0.364	0.782	1.315	1.007	2.13
9	360.2	0.574	0.476	0.403	0.753	1.337	0.994	2.26
10	360.9	0.534	0.446	0.436	0.731	1.356	0.974	2.38
11	361.9	0.498	0.413	0.467	0.711	1.381	0.941	2.48
12	363.0	0.436	0.358	0.521	0.660	1.436	0.948	2.51
13	364.3	0.387	0.319	0.562	0.624	1.463	0.928	2.62
14	365.3	0.346	0.285	0.595	0.584	1.489	0.933	2.65
15	366.5	0.319	0.257	0.624	0.552	1.510	0.915	2.63
16	367.6	0.295	0.243	0.637	0.539	1.508	0.886	2.79
17	368.5	0.269	0.219	0.661	0.506	1.534	0.885	2.79
18	369.8	0.246	0.198	0.684	0.481	1.556	0.855	2.85
19	371.3	0.224	0.167	0.712	0.456	1.675	0.816	2.90
20	372.5	0.177	0.143	0.739	0.394	1.635	0.839	3.03
21	373.9	0.157	0.126	0.754	0.362	1.631	0.824	3.05
22	375.2	0.143	0.109	0.772	0.343	1.723	0.792	3.12
23	376.9	0.000			0.000			

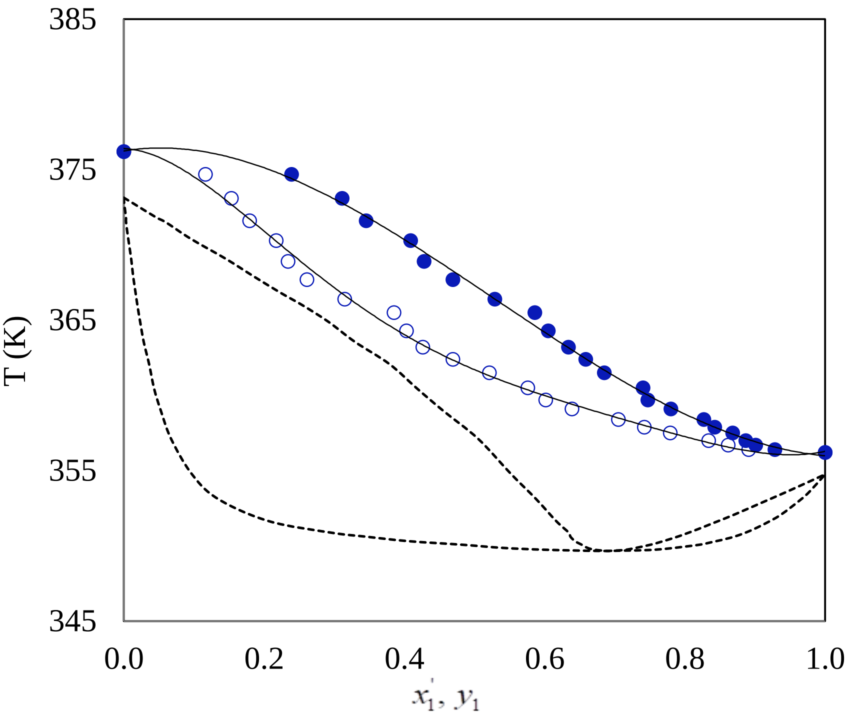
Standard uncertainty $u(x_1) = u\ (x_1) = u(y) = 0.003, u\ (T) = 0.1K, u\big(mole\ \%\ of\ EC\ (2:1)\big) = 0.1, u(\alpha) = 0.025.$ *x_1 is mole fraction of ACN in liquid phase expressed on DES free basis*

From **Figure 4.3 (a), (b), (c),** it has been proved that EC (2:1) generates an excellent salting-out effect on the ACN(1) + water(2) azeotropic mixture. **Figure 4.3** shows that there is an increase in the equilibrium temperature of the system by incorporation of DES into the azeotropic mixture. As the amount of DES increases the equilibrium temperature for system also increases.



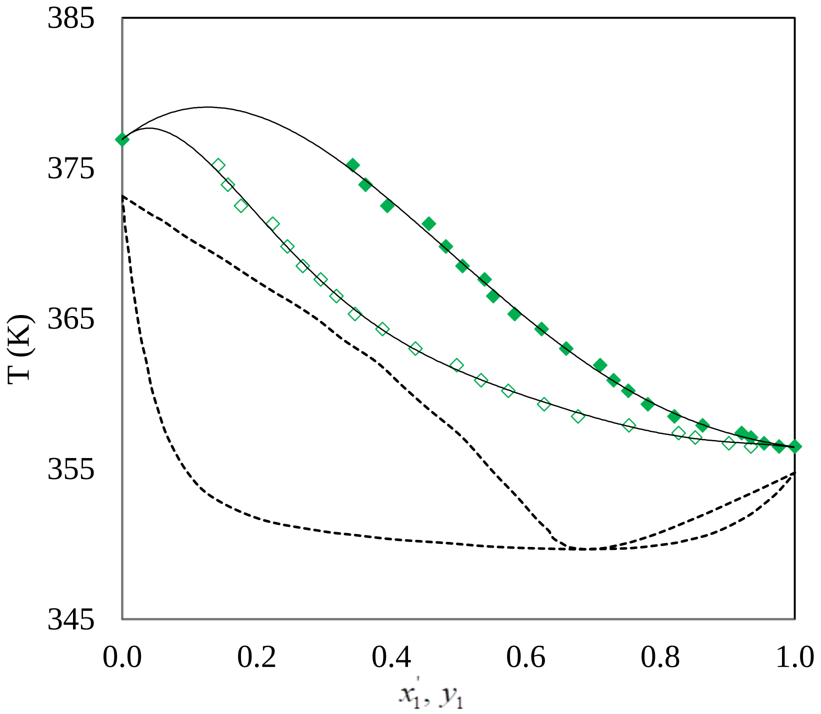
(a)

Figure 4.3 (a): Temperature−composition diagram for the acetonitrile (1) + water (2) + EC2:1 (3) system at 101.3 kPa with EC2:1= 5 mol%. $x_1^{'}$ vs T (Δ) and y_1 vs T (▲), --- EC2:1= 0 %.



(b)

Figure 4.3 (b): Temperature–composition diagram for the acetonitrile (1) + water (2) + EC (2:1) (3) system at 101.3 kPa with EC2:1= 10 mol%. x_1'vs T (○) and y_1 vs T (●), --- EC2:1= 0%.



(c)

Figure 4.3 (c): Temperature−composition diagram for the acetonitrile (1) + water (2) + EC (2:1) (3) system at 101.3 kPa with EC2:1= 12 mol%. x_1'vs T (□) and y_1 vs T (■), --- EC2:1=

The equilibrium diagram for the above experimentations are also represented in **Figure 4.4**. The effectiveness for different DES dosage is clearly evident in the figure. At 5 mol % EC2:1 could not break the azeotrope sucessfully but a clear shift in azeotropic point could be observed which is shown in **Figure 4.4**. It is visible from the figure that at higher DES dosage (>5 mol%) a clear azeotrope break was observed. This study proves that used DES (EC2:1) is an efficient component for the braeking of ACN-Water azeotropic blend.

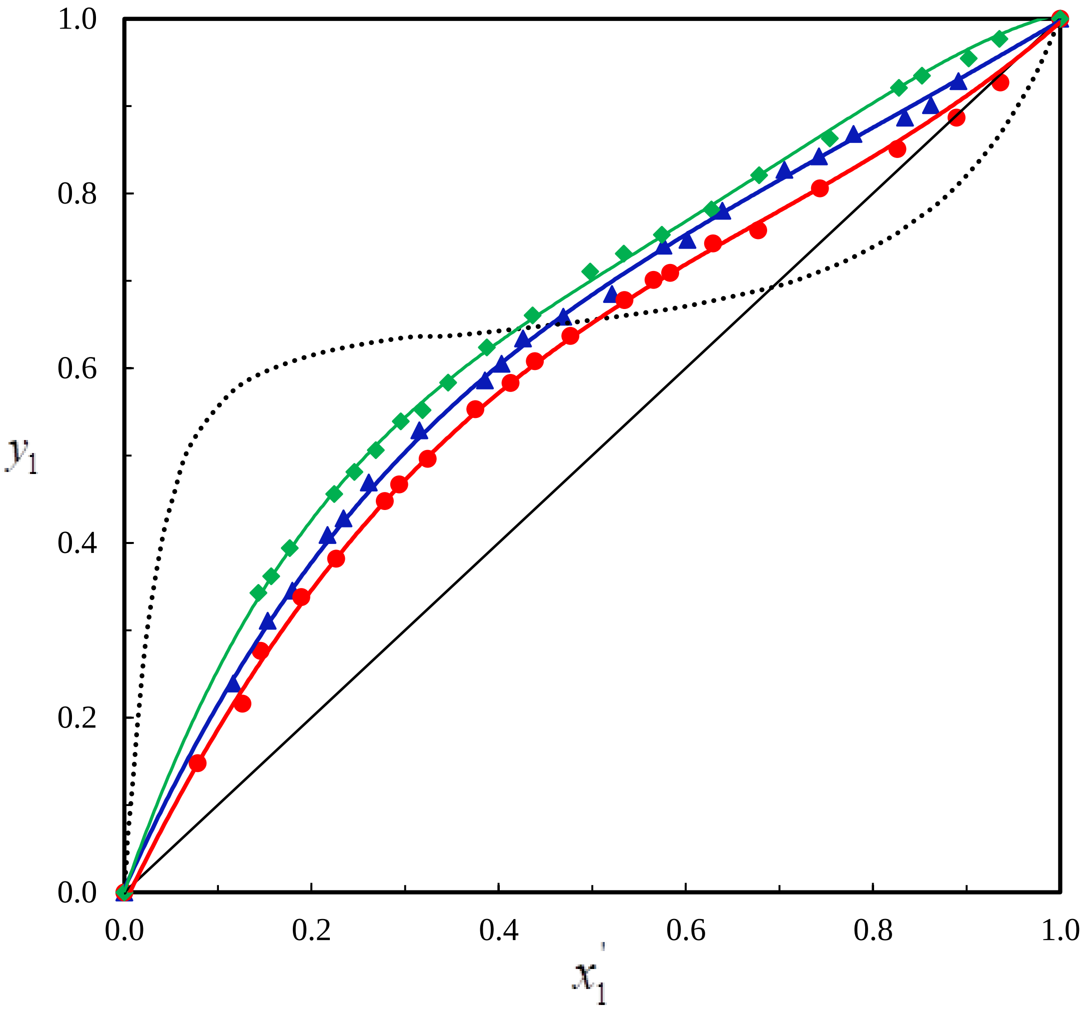


Figure 4.4. Experimental and calculated VLE data for the ACN (1) +water (2) + EC2:1 (3) pseudo ternary system at 101.32 kPa. For EC2:1 = 5 mol% (●), for EC2:1= 10 mol% (▲), for EC2:1= 12 mol% (◆), and solid lines, calculations based on the NRTL model.

4.3 Correlation of VLE data

VLE is calculated from the fugacity equality in vapor and liquid phases, as given in Eq. (1).

$$\hat{f}^V = \hat{f}^L \tag{1}$$

Using the $\gamma - \varphi$ approach, the equilibrium Eq. (2) is obtained.

$$y_i\, \hat{\varphi}^V p = x_i\, \gamma_i\, p_i^s\, \varphi_i^s\, PE_i \tag{2}$$

where $\hat{f}^V$ (vapor phase) and $\hat{f}^L$ (liquid phase) are fugacities of i^{th} component , y_i (vapor phase) and x_i (liquid phase) are the mole fraction of i^{th} component , P is the total system pressure, φ_i^V represents the fugacity coefficient of i^{th} component (vapor phase), γ_i is the activity coefficient for i^{th} component (liquid phase), φ_i^S is fugacity coefficient at saturation condition and system temperature and p_i^s is the vapor pressure of i^{th} component at saturation condition and system temperature. p_i^s was evaluated using Antoine equation and equation parameters were taken from the literature [22].

Fugacity coefficients were evaluated by employing virial equation of state reduced at the second coefficient with Tsonopoulo correlations [23]. Saturated liquid molar volumes and vapor pressures essential for calculation of Poynting effect (PE) were estimated with the help of DIPPR equations [24].

$$PE_i = \exp\left[\frac{v_i^L\left(p - p_i^s\right)}{RT}\right] \tag{3}$$

So, the activity coefficients can be expressed as following:

$$\gamma_i = \frac{y_i\, \hat{\varphi}^V\, p}{x_i p_i^s\, \varphi_i^s\, PE_i} \tag{4}$$

The value of PE ≈ 1 at low/moderate pressure. Thus above equation should be written simply as:

$$y_i\, \hat{\varphi}_i^V p = x_i\, \gamma_i\, p_i^s\, \varphi_i^s \tag{5}$$

EC2:1 is a non- volatile substance and will disappear in the gaseous phase. However, in the liquid phase, EC2:1 mole fraction was considered for calculating the activity coefficients of both the compounds. Experimental activity coefficients were determined using above equation and were correlated with the values obtained from the NRTL model.

The model parameters were regressed by minimizing the following objective function [25].

$$OF = \sum_{i=1}^{n}\left[\frac{\gamma_i^{\exp} - \gamma_i^{calc}}{\gamma_i^{\exp}}\right]^2 \tag{6}$$

where, i and n defines to the component and experimental data point respectively.

The relative volatility (α_{12}) were evaluated by

$$\alpha_{12} = \frac{y_1 / x_1^{'}}{y_2 / x_2^{'}} \tag{7}$$

where $x_1^{'}$ and $x_2^{'}$ are ACN and water mole fractions (liquid phase) represented on EC2:1-free basis, respectively, and y_1, y_2 are the mole fractions of ACN and water (vapor phase), respectively.

It can be noticed via results that, the assumed values from NRTL model provided good correlation with the experimental VLE data as highlighted in Figure 4. The results of correlation for the average difference in T and vapor mole fraction in ternary system are reported in Table 3. The average and maximum difference in T and ACN mole fraction (vapor phase) are defined as following:

$$DT = (1/n)\sum_{k=1}^{n} \left| T^{\exp} - T^{cal} \right|_k \tag{8}$$

$$dT = \max\left(\left| T^{\exp} - T^{cal} \right| \right) \tag{9}$$

$$Dy_1 = (1/n)\sum_{k=1}^{n} \left| y_1^{\exp} - y_1^{cal} \right|_k \tag{10}$$

$$dy_1 = \max\left(\left| y_1^{\exp} - y_1^{cal} \right| \right) \tag{11}$$

Where "n" highlights the quantity of data points and "exp" as well as "cal" represent the experimental along with calculated values respectively. The average absolute difference for the temperature and ACN mole fraction (vapor phase) are 0.36 K and 0.015 respectively.

Table 7. The parameters and correlation deviations of NRTL model at 101.32 kPa.

Systems	Δg_{12}	Δg_{21}	α	$DT(K)$	$dT(K)$	Dy_1	dy_1
ACN (1)+EC2:1 (2)	7295.6	-1207.5	0.3	0.010	0.260		
Water (1)+EC2:1 (2)	8039.2	-1834.4	0.3	0.003	0.24		
ACN (1)+water (2) + EC2:1 (3)	3237.1	-1354.8	0.3	0.36	0.62	0.005	0.015

$$\Delta g_{12} = (g_{12} - g_{22})$$

$$DT = (1/n)\sum_{k=1}^{n} \left| T^{\exp} - T^{cal} \right|_{k}$$

$$dT = \max\left(\left| T^{\exp} - T^{cal} \right| \right)$$

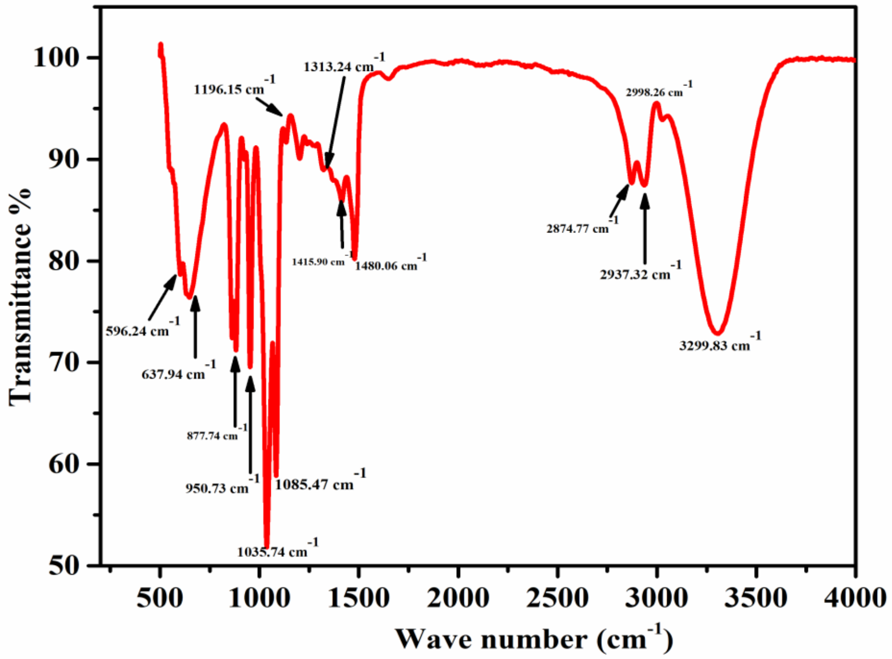
$$Dy_1 = (1/n)\sum_{k=1}^{n} \left| y_1^{\exp} - y_1^{cal} \right|_{k}$$

$$dy_1 = \max\left(\left| y_1^{\exp} - y_1^{cal} \right| \right)$$

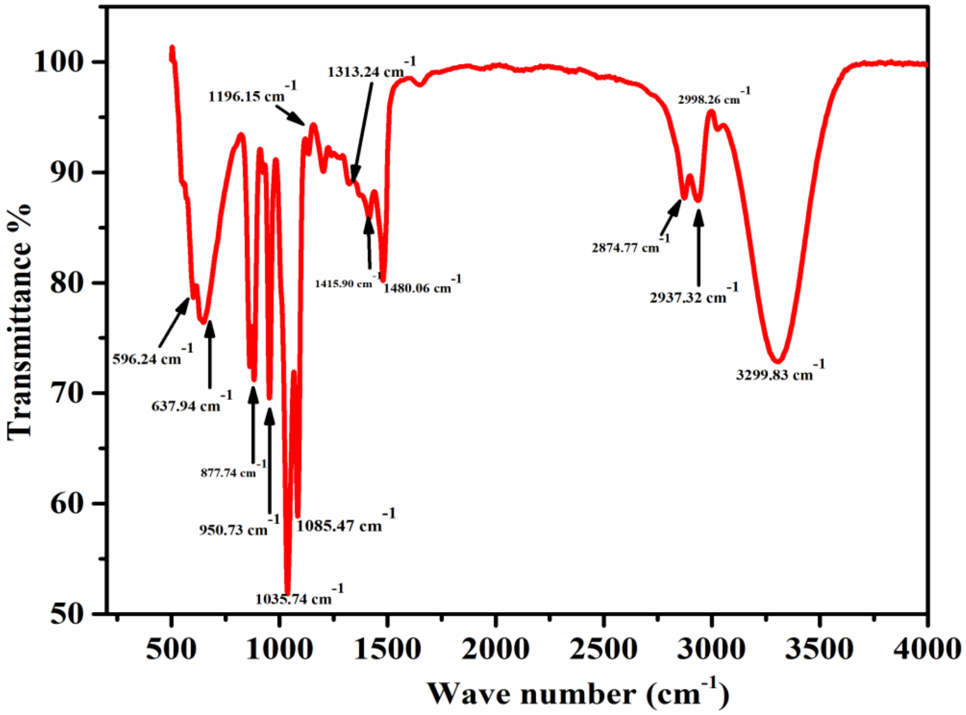
4.4 Recovery of used DES

To maintain the economy in extractive distillation, solvent should be reusable. In order to check the reusability of the DES (EC 2:1), it was recovered from the bottom product. In this process, mixture was boiled for 2.5 h and was kept in vacuum evaporator overnight. This recovered DES was analysed using FTIR for any chemical change. In **figure 4.5** FTIR of freshly prepared and recovered EC 2:1 is shown for comparison. The spectra of both FTIR represents that there is no significant change and the chemical properties of recovered EC 2:1 remains stable. Hence, EC 2:1 can be reused for further experiments.

Figure 4.5 FT-IR spectrum of (EC2:1) i. Pure DES ii. Recovered DES



(i)



(ii)

CHAPTER 5 Conclusion

A modified Othmer recirculation still was taken for quantifying the VLE data. In case of pseudo binary system DES EC(2:1) + water, DES EC(2:1) + ACN at room temperature the VLE data was calculated and for pseudo ternary system DES EC(2:1) + ACN + water the VLE data was computed at different DES mol % and these are- 5%, 10%, 12%. From this study, it has been found that EC (2:1) is a remarkable component in the break- down process of ACN + water azeotropic blend. As compare to conventional solvents used previously, the solvent requirement in this separation is higher, but EC (2:1) has the ability to successfully break the ACN + water azeotrope. As it has been already known that the conventional solvents are toxic in nature but the solvents used in this study i.e. the deep eutectic solvent(EC) are environment friendly hence are non-toxic but still there is a need to explore different deep eutectic solvents for the separation of such azeotropic mixtures.

List of symbols

A_i, B_i, C_i	Antoine equation constants of component i
OF	Objective function
g	Interaction parameters in NRTL equation, J/mol
P	Total pressure in the system, kPa
p_i^{sat}	Saturation vapor pressure of pure liquid i, kPa
x_i	Mole fraction of component i in liquid phases
$x_i^{'}$	Mole fraction of component i in the liquid phase on DES-free basis
y_i	Mole fraction of component i in vapor phases
T	Equilibrium boiling temperature, K
T_b	Boiling points of pure substance at 101.32 kPa, K
V^L	Liquid molar volume

Acronyms

DES	Deep eutectic solvent
VLE	Vapor–liquid equilibrium
FTIR	Fourier transform infrared spectroscopy
ACN	Isopropyl alcohol

Greek letters

α	Non-randomness parameter in NRTL equation
α_{12}	Relative volatility of component 1 and 2
γ_i	Activity coefficient of component i in the liquid phase
ϕ_i^V	Fugacity coefficient of component i
ϕ_i^S	Fugacity coefficient of saturated pure i

Superscripts

cal	Calculated value

exp	Experimental value
L,V	In the liquid phase; in the vapor phase

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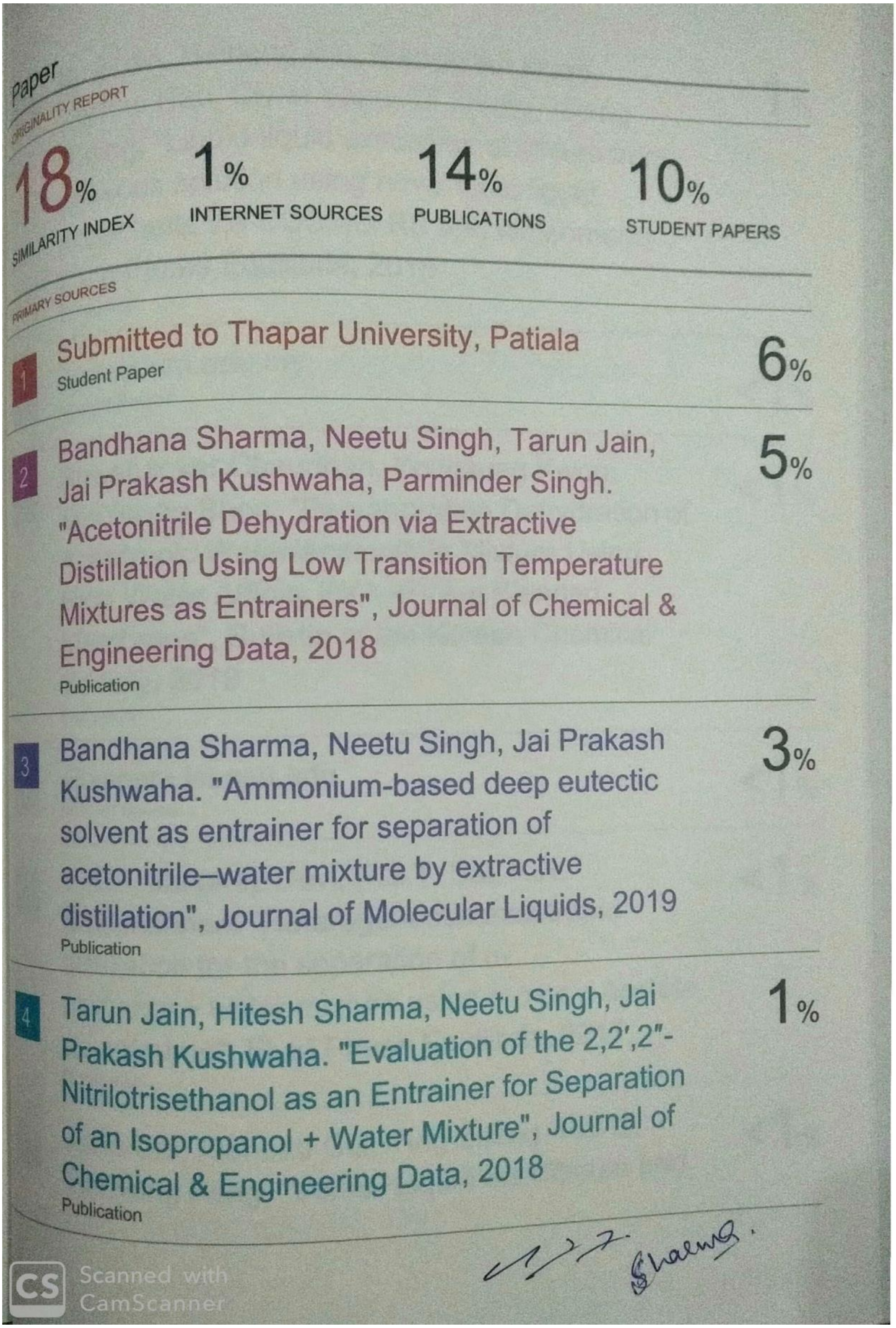

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